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SULFUR LINKAGE IN VULCANIZED RUBBER

REACTION OF METHYL IODIDE WITH SULFUR COMPOUNDS *

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The work described here is an extension of the study of the reaction of methyl iodide with sulfur compounds originally begun with the purpose of using such data in determining the sulfur linkage in vulcanized rubber. A previous paper[1] dealt with the reactions of methyl iodide with propanethiol, propyl sulfide, propyl disulfide, allyl sulfide, and thiophene. This article adds to the list, n-butyl methallyl sulfide, allyl disulfide, allyl tetrasulfide, n-propyl tetrasulfide, and trithiane.

The removal of combined sulfur from vulcanized rubber as trimethyl-sulfonium iodide on treatment with methyl iodide at room temperature[2] was persuasive evidence of the presence of sulfide sulfur linked to allylic type residues. The evidence offered, however, did not constitute exclusive proof because it was not known whether still other types of sulfur linkage would also yield trimethylsulfonium iodide. To shed more light on this question, the sulfur linkages most likely to occur in vulcanizates—the allyl-alkyl mono-sulfide, diallyl and dialkyl di- and polysulfide—were investigated. The trithiane reaction is of interest mostly from the point of view of the reaction of overcured stocks or secondary reaction products stemming from the original polysulfides. The reactions were carried out using the method described in a previous paper[1].

n-BUTYL METHALLYL SULFIDE

This compound was synthesized from butanethiol and methallyl chloride by the same method that Bost and Conn[3] used for propyl sulfide. The reaction mixture was heated 4 hours instead of the recommended 8 hours which resulted in increasing the yield from 50 to 80 per cent. The crude dry product was fractionated through a 25-plate helix-packed column to give a product with the constants shown in Table I.

The best fractions were used for the methyl iodide reaction. The reaction is rapid. A yellow layer of product forms on top of the mixture within 2.5 hours and in 20 hours the reaction is complete. The excess methyl iodide is evaporated at room temperature in vacuo and the oily cream-colored solid taken up in the least possible alcohol. After precipitation with ether at 0° C and repetition of the solution and precipitation, there are obtained white crystals, melting point 83.5° C, 13.25 per cent sulfur; calculated for $(CH_3)_2C_4H_9SI$, 13.0 per cent. This compound is very hygroscopic and should be kept in a desiccator.

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The reaction to produce dimethyl n-butylsulfonium iodide and not methyl n-butylmethallylsulfonium iodide shows definitely that a sulfide linkage alpha to a carbon-carbon double bond is unstable to methyl iodide, whether there are one or two such groups on the sulfur. However, in the presence of methyl iodide over very long periods of time, even alkylsulfonium iodides are unstable. Thus, when the reaction of n-butylmethallyl sulfide is continued over 400 hours at 24° C, the product dimethyl-n-butylsulfonium iodide gives rise to trimethyl sulfonium iodide until at 1200 hours the product is 25 per cent trimethyl-sulfonium iodide. This instability is again illustrated by the fact that the normal reaction of n-propyl disulfide yields dimethyl-n-propylsulfonium iodide but the latter product on standing 2 years in contact with methyl iodide is completely converted to trimethylsulfonium iodide.

The reaction of n-butylmethallyl sulfide to give trimethylsulfonium iodide can be accelerated by heat. In 15 hours at 50° C, a 25 per cent yield of trimethylsulfonium iodide is produced; the remainder is the normal product, dimethyl n-butylsulfonium iodide. Bloomfield[4] and Farmer and Shipley[5] have recently indicated that propylallyl sulfide, dihydromyrcene cyclic sulfide, and

TABLE I
PHYSICAL PROPERTIES OF PURIFIED COMPOUNDS

Compound	Color	B.P. (° C)	Pressure (mm. Hg)	n_4^{25}	d_D^{20}
n-Butyl methallyl sulfide	Colorless	182.7	749.8	1.4656	0.8592
		90.4	42.0	1.4685[a]	0.8546[b]
Allyl disulfide	Slightly yellow	74.8	13.8	1.5312	0.9919
Propyl tetrasulfide	Light yellow	>45	0.001	1.5993	..
Allyl tetrasulfide	Light yellow	>45	0.001	1.6360	..

[a] At 20° C.
[b] At 25° C.

cyclohexylcyclohexenyl sulfide all form adducts with methyl iodide but not trimethylsulfonium iodide. Their experiments must be interpreted as applying only to relatively short reaction times at room temperature.

ALLYL DISULFIDE

Several commercial sources of allyl disulfide were investigated. These products on analysis by fractional distillation proved to be mostly allyl sulfide with di- and polysulfides. The compound therefore was synthesized by the method of Twiss as modified by Westlake and Dougherty[6]. This method involves the preparation of the Bunte salt with subsequent oxidation using hydrogen peroxide.

The dry crude product was distilled at 13 mm. mercury pressure in a helix-packed column. The distillation was not satisfactory as bumping was frequent. There were indications that even at the low pot temperature used (110° C) there was decomposition. The constants of the best fraction are shown in Table I. The product had sulfur 41.0%; calculated for $C_6H_{10}S_2$, 43.8%. On standing, a slight cloudiness developed in a few days, while the refractive index at 25° C changed in 4 weeks from 1.5312 to 1.5271. The samples were sealed in vacuo after distillation and kept at 0° C until used.

The best fraction of allyl disulfide was reacted with methyl iodide in ethanol in the dark at 24° C under nitrogen. The mixture turned yellow after 24 hours, and crystals of trimethylsulfonium iodide appeared in 7 days. An attempt was

made to follow the reaction by titrating the free iodine with aqueous thiosulfate in the presence of alcohol. Even after 400 hours reaction time the free iodine was only 10 per cent of the theoretical yield despite actual isolation of trimethylsulfonium iodide indicating yields of 35 per cent. The iodine liberated is probably used up by addition at the double bonds in the allyl residue. This isolation of trimethylsulfonium iodide shows that the reaction goes 35 per cent to completion in 400 hours as shown in Equation 2:

$$C_3H_5-S_2-C_3H_5 + 4CH_3I \rightarrow 2(CH_3)_2C_3H_5SI + I_2 \tag{1}$$

$$(CH_3)_2C_3H_5SI + CH_3I \rightarrow (CH_3)_3SI + C_3H_5I \tag{2}$$
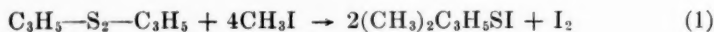
The total weight gained in the reaction calculated as trimethylsulfonium iodide was twice the quantity of trimethylsulfonium iodide actually isolated. Products of the type shown in Equation 1 or others rich in iodine, probably account for this difference. This reaction is still very slow compared to the sulfide reaction. As iodine is liberated, the reaction of allyl disulfide follows the disulfide pattern described in Equation 1. But the products still have a sulfur linkage alpha to the double bond, and continue to break down to trimethylsulfonium iodide, as shown in Equation 2. When mercuric iodide is used as a catalyst without ethanol, the reaction mixture turns brown-red, due to iodine, in 4 hours, and a red-brown oil is deposited on the bottom of the flask. The free iodine is again far below that indicated by Equation 1. No solid was present in the reaction mixture. When the methyl iodide was evaporated, a red-brown oil remained. If this is washed with acetone, there is obtained a yellow solid-plastic mass which on shaking gives particles. This solid is peculiar. On standing or vacuum drying, it referts to a red-brown oil. On addition of acetone the yellow solid again is obtained. It is insoluble in alcohol, carbon tetrachloride, benzene, hexane, and chloroform.

This material resembled to a great extent that described later under the allyl polysulfide analogous reaction. Thus mercuric iodide catalyzes the reaction, but the products differ from those of the uncatalyzed reaction.

PREPARATION OF POLYSULFIDES

Polysulfides have been prepared from thiols and sulfur monochloride; alkyl halides and aqueous alkali metal polysulfides; and alkyl halides and anhydrous metal polysulfides. The last method was chosen for the present work inasmuch as there seemed to be the least chance of side reactions because the reaction between anhydrous alkali metal polysulfide and the halide takes place at room temperature. In addition, allyl polysulfide can be prepared by this method, whereas the sulfur monochloride method affects the double bonds, and the aqueous alkali metal polysulfide method does not give allyl polysulfide.

Potassium pentasulfide was prepared by the method of Rule and Thomas[7], isolated, and stored over barium oxide.

Following the method of Riding and Thomas[8] the pentasulfide was reacted in ether with the appropriate halide, in this case, propyl iodide. A convenient modification involves using 500-cc. Pyrex glass-stoppered bottles with quartz pebbles. These are filled with the reaction mixture, blown out with nitrogen, and put on ball-mill rollers for several days. The yield of crude dry propyl pentasulfide was 59 per cent in 5 days. Allyl pentasulfide was prepared from allyl bromide in the same fashion—yield 70 per cent in 4 days. The crude

products were light yellow mobile liquids which did not deposit sulfur on standing at 0° C for 30 days.   Both products were distilled in a simple molecular still at low temperatures.   The polysulfide fractions used were those corresponding to the tetrasulfides which distilled over at under 45° C.   Both allyl and propyl pentasulfides were found to be mixtures.   About 50 per cent of each product was polysulfide from —S_3— to —S_6—.   The best fraction of each corresponding to the tetrasulfides had the properties shown in Table I.   Bezzi[9] gave n_D^{20} 1.5904 for propyl tetrasulfide made from propanethiol and sulfur monochloride.   Thomas and Riding[10] have discussed the preparation and some chemical reactions of allyl pentasulfide made by the above method. n-Butyl polysulfide and methallyl polysulfide were prepared by the present authors in the same fashion from n-butyl bromide and methallyl chloride, respectively.

An unpublished procedure of Horst and Striegler[11] was also tried for the preparation of allyl pentasulfide.   This method which consists of reacting methallyl chloride with aqueous ammonium polysulfide, yielded a product which, both in the crude state and after molecular distillation, deposited sulfur on standing at 0° C.   This procedure is not so satisfactory as the anhydrous alkali polysulfide method.

PROPYL TETRASULFIDE

The reaction of propyl tetrasulfide with methyl iodide at 24° C in nitrogen resulted in about 5 per cent weight gain in 500 hours.   The samples turned yellow in 18 hours, deposited traces of trimethyl sulfonium iodide in 200 hours, and turned orange from 200 to 350 hours and red-brown at 500 hours.   If the entire weight gain is assumed to be due to conversion to trimethylsulfonium iodide, then less than 1 per cent of the sulfur reacted.

At 55° C in vacuo there was a 9 per cent weight increase in 66 hours.   The reaction mixture was orange, with needles of trimethylsulfonium iodide floating therein.   Sufficient of the sulfonium salt was isolated to account for only 2 per cent conversion.   A small amount of rhomboid sulfur was also isolated.   Evidently the small amount of reaction results in cleavage of the polysulfide linkage, with formation of the trimethylsulfonium iodide as well as liberation of some of the sulfur as the free element.

The only work in the literature (to the author's knowledge) on the reaction of methyl iodide on organic polysulfides is that of Davies[12], who isolated trimethylsulfonium iodide from the 4-hour reaction with methyl trisulfide at 100° C.   Farmer and Shipley[5] erroneously refer to the work of Rây and Adhikari[13] as bearing on the fission of polysulfide links by methyl iodide alone at room temperature, whereas the latter authors studied only the mercuric iodide-catalyzed reaction at elevated temperatures.

The mercuric iodide catalyzed reaction was studied at 24° C in nitrogen. The reaction mixture turned red-brown in 2 hours, and after 24 hours a yellow-brown oil was deposited on the flask bottom.   After 250 hours the weight gain (nonvolatile products) was 125 per cent.   A yellow crystalline product was isolated in 30 per cent yield by solution in acetone followed by precipitation by ether; yellow crystals, melting point 62.5° to 63.0° C, carbon 8.92 per cent hydrogen 2.05 per cent; calculated for $(CH_3)_2C_3H_7SI \cdot HgI_2$, carbon 8.75 per cent; and hydrogen 1.90 per cent.   This compound is new as far as could be ascertained.   The polysulfide linkage is thus broken by methyl iodide–mercuric iodide but no trimethylsulfonium iodide complex is formed.

ALLYL TETRASULFIDE

In general the action of methyl iodide on allyl tetrasulfide resembles very closely that on propyl tetrasulfide. In 18 hours the reaction mixture was yellow, turning to gold with increasing reaction time, and finally to yellow-orange at 500 hours. The color was always lighter than the corresponding propyl tetrasulfide reaction mixtures, probably because of absorption of the liberated iodine by the bonds. The weight gain of the reaction was about 2 per cent. Crystals of trimethylsulfonium iodide were visible after 200 hours but only about 1 per cent of the theoretical yield was isolated. In both the propyl and allyl tetrasulfide methyl iodide reactions, the evaporation of the methyl iodide gave the original tetrasulfide, a very small amount of iodine or very dark immiscible phase, and a small quantity of trimethyl sulfonium iodide.

When the reaction was carried out at 55° C in vacuo, there was obtained a 6 per cent yield of trimethylsulfonium iodide (calculated on available sulfur), some free iodine, and a small quantity of free sulfur. More trimethylsulfonium iodide was formed than in the corresponding experiment with propyl tetrasulfide.

Mercuric iodide catalyzes the reaction so that in 2 to 3 hours at 24° C the reaction mixtures turn red-brown. A brown oil is deposited on the bottom of the flask after 24 hours. In 250 hours the weight gain is 150 per cent. After evaporation of the methyl iodide a red-brown oil is left. If this is shaken with acetone, a gummy yellow mass is formed which at 0° C breaks up into particles. These particles resemble to a great extent the corresponding product from allyl disulfide. No definite melting point is obtained, although the color changes to orange above 95° C and to red about 120° C, with melting. The material has 28.1 per cent sulfur and, therefore, is not the expected sulfonium–HgI_2 complex.

TRITHIANE

The reaction of trithiane or thioformaldehyde with methyl iodide was studied as early as 1877, when Klinger[14] found that trimethyl sulfonium iodide was produced when the reaction was carried out either at room or at elevated temperatures. He was puzzled to account for the fact that only 1 molecule of the sulfonium compound was produced for each molecule of trithiane. These observations were confirmed by Reychler[15] in 1905 who in agreement with Klinger wrote the equation:

$$C_3H_6S_3 + 3CH_3I \rightarrow (CH_3)_3SI + C_3H_6S_2I_2$$

However no experimental proof was offered for the existence of the $C_3H_6S_2I_2$ compound.

In 1939 Lee and Dougherty[16] made a monomethyl iodide derivative of trithiane through dimethyl sulfate and potassium iodide. This compound melting point 124° to 126° C[17] had the formula $C_4H_9IS_3$, with correct sulfur and iodine analyses as well as molecular weight.

The reactions described here were carried out in ethanol at 24° C under nitrogen in the dark. Eastman trithiomethylene (White Label) was purified by recrystallization from hot benzene—melting point 217.5° C. When the reaction had continued for 60 hours, crystals appeared which were removed after a 288-hour period. Weight gain data indicated 100 per cent reaction, $3CH_3I$ adding for each $C_3H_6S_3$. The white needles, melting point 180° to 182° C, contained 15.8 per cent sulfur. They decomposed at the melting point

to a red liquid, with evolution of gas. The compound is not stable on standing in air. However, the white crystals obtained from the reaction mixture at 500 hours decomposed without melting at 202° C. This behavior is characteristic of $(CH_3)_3SI$.

COMPLEXITY OF THE METHYL IODIDE—VULCANIZATE REACTION

A summary of the methyl iodide reactions is given in Table II. It can be seen that the reaction to give trimethylsulfonium iodide goes very slowly and is, at least in the first 160 hours, negligible. Yet in that same time span the rubber-sulfur stock SB1A had already lost 80 per cent of the entire amount

TABLE II

PRODUCTION OF TRIMETHYL SULFONIUM IODIDE BY SULFUR COMPOUNDS AT 24° C

Compound	First appearance of $(CH_3)_3SI$ (hours)	$(CH_3)_3SI$ yield Time (hrs.)	(%)
n-Butyl methallyl sulfide	400	1200	25
Allyl disulfide	168	400	35
Propyl tetrasulfide	200	500	1
		66	2[a]
Allyl tetrasulfide	200	500	1
		66	6[a]
Trithiane	>300	500	>50

[a] At 55° C.

of sulfur that is eventually eliminated[2]. For this reason, it is unlikely that any of the types of sulfur linkage studied here is responsible for the production of the sulfonium salt in the first 160 hours of the methyl iodide–vulcanizate reaction. When reaction times over 160 hours are considered, all the linkages may contribute small amounts of trimethylsulfonium iodide, except that the polysulfides studied react very slowly.

The experiments described in a previous paper[2] did not show that all the sulfur removable from the methyl iodide-treated vulcanizate was in the form of trimethylsulfonium iodide. The reacted vulcanizate was always acetone-extracted. This extraction probably decomposed those sulfonium compounds whose hydrocarbon residues were the rubber chains and were therefore not removable as such. Future investigation should distinguish between the sulfur removed as trimethylsulfonium iodide and as decomposition products of other sulfonium iodides and as decomposition products of other sulfonium salts. This could be accomplished by the initial use of cold extraction with chloroform or isopentane, followed by hot acetone extraction. Analysis of the vulcanizate at each stage would provide the necessary data. Only the sulfide type of linkage reacts fast enough to give an appreciable amount of any sulfonium salt in the initial period of 160 hours. Trithiane is considered to be a special case of the sulfide type link. It is possible, therefore, that the unstable sulfonium salts whose origins are the dialkyl and allyl-alkyl type sulfide linkages, as well as the trimethylsulfonium iodide from the diallyl type, are concerned in the removal of combined sulfur from the vulcanizate.

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SULFUR LINKAGE IN VULCANIZED RUBBER
ACETONE EXTRACTION OF VULCANIZATES *

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Study of the olefin-sulfur system in the attempt to gain insight into the chemistry of sulfur vulcanization is now firmly established[1]. This method has yielded much valuable information. However, the ultimate test of the analogy is its ability to explain the properties of vulcanized rubber. Every effort should be made, therefore, to obtain experimental verification of facts ascertained on the simpler analog, using the vulcanizate itself.

The experiments with the model system, 2-methyl-2-butene and sulfur, described by the authors[2] and those of Farmer and Shipley[3] with cyclohexene, showed that in the olefin-sulfur system the main reaction product was of the type R-S$_x$-R, where x was about 6. This nearly exclusive formation of polysulfides does not fit in with the generally accepted concept of the rubber-sulfur system. The following experiments were designed to give some indication of the presence of polysulfide links in rubber-sulfur vulcanizates.

All of the reactions of methyl iodide and vulcanizates so far reported[4] have been carried out with acetone-chloroform extracted stocks. This nearly universal practice of solvent extracting vulcanizates to remove free sulfur needs closer scrutiny. If polysulfides are present their stability in contact with solvents at 57° C may be questioned.

When n-propyl tetrasulfide was refluxed with acetone for 24 hours, 20 per cent of the sulfur above the disulfide level was liberated as free sulfur. This same experiment was repeated with allyl tetrasulfide and a polysulfide from the olefin-sulfur reaction. Surprisingly enough, no free sulfur was found in these experiments. Thus, hot acetone may liberate sulfur from some polysulfides. If there is no point of attack on the hydrocarbon residues, this sulfur is removable by the solvent as free sulfur. However, the liberated sulfur may combine with any unsaturated residues to give more stable types of sulfur linkages than polysulfides. This reaction may be reflected in changes in the physical properties of the vulcanizates as well as their chemical behavior.

EFFECT OF EXTRACTION ON COMBINED SULFUR AND TENSILE STRENGTH

A series of extraction experiments was carried out to see if the combined sulfur and tensile properties of a cold-extracted stock differed from a hot acetone-extracted stock.

Standard 6 × 6 inch sheets 0.075 inch thick were extracted 24 hours after vulcanization in a large extractor operating on the A.S.T.M. hot extraction principle, until all free sulfur was removed, usually for 2 weeks. The sheets

were then dried in a vacuum of 10^{-3} mm. mercury for 24 hours at room temperature, and tested immediately on removal from the vacuum.

Combined sulfur, determined as a check on the effect of the treatment, showed little variation. It was necessary to indicate the effect of oxygen by running corollary aging experiments. For this the sheets were glass-sealed in the proper atmosphere (Table I). As very long periods of extraction were used, compared to standard analytical procedures, it is not possible to correlate the data directly with changes that occur on ordinary acetone extraction. However, intercomparison between the different extraction and aging procedures is valid. The loss of tensile strength on acetone extraction is striking—from 3700 to 940 pounds per square inch. Extraction at the same temperature but with a hydrocarbon solvent, 2,3-dimethylbutane, gives the same results. Therefore the nature of the solvent by itself is not a determining factor. If the samples are aged in air and nitrogen, respectively, at 57° C, the former shows a loss of 33 per cent in tensile strength, whereas the nitrogen-aged sample is practically unaffected. Therefore oxygen is necessary for the degradation. When the low boiling hydrocarbon, isopentane (boiling point 29° C), is used, the tensile strength drops only 12 per cent. This shows that the higher temperature is essential to degradation. The net conclusion is that in the extrac-

TABLE I

STRESS-STRAIN PROPERTIES OF RUBBER-SULFUR STOCK SBIA
AS AFFECTED BY EXTRACTION OF DRY AGING

Extraction or aging medium	Temp. (° C)	Time exposed (days)	Tensile stress (lg./sq. in.)	Elonga- tion (%)	Modulus at 600% (lb./sq. in.)	Combined sulfur (%)
Original SB1A (100 rubber, 8 sulfur, 4 hr. at 141.6° C)	..	..	3700	970	480	4.26
Acetone	57	16	940	940	360	4.27
2,3-Dimethylbutane	58	14	520	800	200	..
Isopentane	29	14	3240	960	480	4.32
Nitrogen	57	16	3300	940	340	4.35
Air	57	16	2100	770	600	4.54

tion of rubber-sulfur stocks with acetone, for extended periods of time, considerable degradation (as shown by loss of tensile strength) takes place; at least a part of this is caused by the action of oxygen at the elevated temperature used. The combination of elevated temperature and access to oxygen is necessary for degradation. The degradation is not due to the specific nature of the solvent because acetone and 2,3-dimethylbutane give identical results.

The polysulfide links, if present, showed the same behavior, as regards conversion to free sulfur, to isopentane at 29° C as to acetone and 2,3-dimethylbutane at 57° C. The presence of the system, polysulfides → extractable free sulfur, at least in the rubber (8 parts sulfur stock SB1A) is, therefore, not indicated by the experiments.

The low temperature extraction of soft rubber vulcanizates with isopentane offers interesting possibilities. As shown in Figure 3, the isopentane free sulfur values check those obtained with acetone in the standard 24-hour period. Special extractors, in principle the same as the A.S.T.M. acetone-extraction type, are used. These have ground joints with water-jacketed air vents instead of the rather hit-or-miss closure of the A.S.T.M. type. Using cooling water at 21° C in the summer, a 24-hour extraction can be carried out with only 15 per cent loss of solvent. Thus by use of isopentane, specimens of vul-

canizates suitable for tensile testing can be obtained; these are free of uncombined sulfur and contain very little of the natural antioxidant present in pale crepe.   This last point was indicated by the fact that after standing 36 hours in air, the tensile strength of a sheet of SB1A stock that had been extracted with isopentane, dried, and tested, dropped from 3240 to 300 pounds per square inch.

A procedure for the testing of antioxidants in vulcanizates, in the absence of free sulfur and natural antioxidants, would be made possible by extracting the stock with isopentane; careful drying in high vacuum; weighing, followed by swelling in a solution containing the antioxidant; redrying; and weighing. The sample could then be exposed to oxidation conditions and tested as in conventional procedures.   The advantage would be that natural antioxidants and free sulfur effects would not mask the results.

INFLUENCE OF EXTRACTION ON THE METHYL IODIDE REACTION

Even if the extraction-aging experiments did not give any unequivocal evidence for hot solvent labile polysulfide sulfur, further experiments in this direction were undertaken, because, even if the polysulfide sulfur were labile at room temperature, there is no assurance that it would be extractable.   Presumably the sulfur so liberated would be extremely active and could combine with the rubber before it could be removed.   This possibility was investigated by carrying out the methyl iodide reaction with extracted and unextracted SB1A.

The reaction curves are shown in Figures 1 and 2 in terms of the combined sulfur left in the vulcanizate after methyl iodide treatment.   The data for runs 14 and 26 are taken from previous work[4].   A common ordinate of 4.24 per cent sulfur, at zero time, is assumed for the unextracted stocks to simplify the graph. It is significant that both the uncatalyzed and catalyzed reaction curves of extracted stock SB1A show faster reaction than the unextracted.   This difference is especially marked in the mercuric iodide reaction where only 1.5 per cent sulfur is left in the extracted sample as against 3.0 per cent for the unextracted.

This behavior could be explained in the following way.   If polysulfides were present in the original unextracted vulcanizate, they would react only
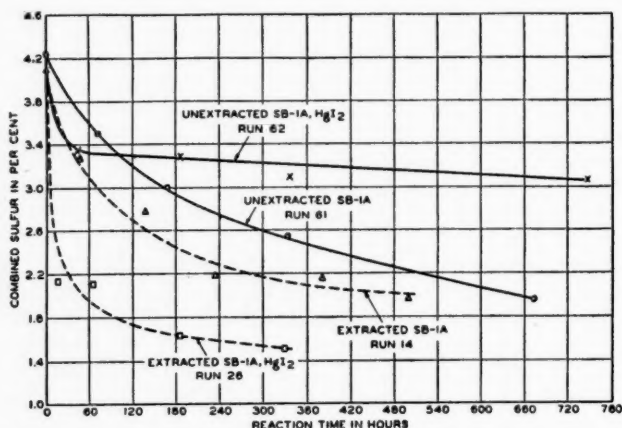
Fig. 1.—Effect of extraction on reaction of methyl iodide with SB1A at 24° C.

slowly with methyl iodide at 24° C[2].   On extraction with acetone the poly-sulfides in the vulcanizate might decompose, giving an active form of sulfur which would react with the rubber to form a type of linkage more readily reactive to methyl iodide than the original polysulfide.   In the mercuric iodide reaction on the unextracted stock the reaction proceeds rapidly to break the polysulfide chains and give a product which is either removable from the rubber at room temperature during the reaction or, on extraction with acetone, only
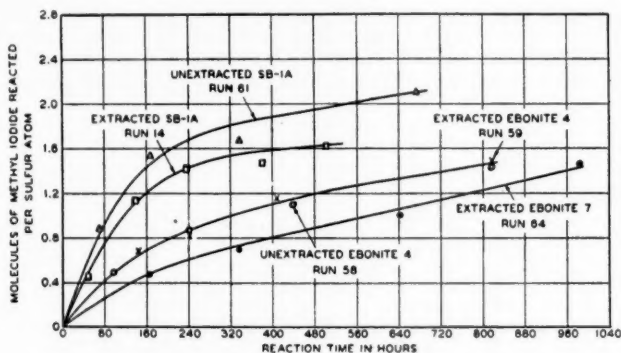
FIG. 2.—Reaction of methyl iodide with SB1A, ebonite 4, and ebonite 7 on total weight gain basis at 24° C.

if the polysulfide is of the dialkyl type.   If the polysulfide is of the diallyl type, resulting products may not be removable from the rubber.   This latter be-havior is shown by reaction of allyl tetrasulfide to give insoluble complex products as described in a previous article[5].   The methyl iodide experiments thus give some indication that even mild treatment, such as hot solvent ex-traction of a rubber-sulfur vulcanizate, may alter sulfur linkages, presumably of the polysulfide type.

COMBINED SULFUR IN EBONITE

The search for polysulfide linkages was carried over into the hard rubber field with the comparison of acetone and isopentane extraction, combined sulfur determination, and methyl iodide reaction of extracted and unextracted ebonites.

The isopentane extraction of the natural rubber ebonites listed in Table II is shown in Figure 3.   The combined sulfur of the extracted, vacuum dried ebonites, whether acetone or isopentane extracted, agree as long as the sulfur content of the stock is 32 per cent or below.   In the case of ebonite 5 (38 per cent sulfur) and ebonite 6 (45 per cent sulfur) the values diverge.   Extension of acetone extraction of ebonite 6 causes a drop of only 1.7 per cent in 400 hours, so only the 72-hour values are given for acetone.   Isopentane does not extract sulfur from ebonite with the speed of acetone, even when the final values are in agreement.

Complete analytical data are given in Table II for the seven ebonites studied.   There are several interesting conclusions that may be drawn.   The acetone-extraction free sulfur method checks with the sodium sulfite method only with undercured ebonites.   The latter method is not even self-consistent

TABLE II
DETERMINATION OF SULFUR IN EBONITES

Ebonite No.	Type	Cure at 298° F (hr.)	Total sulfur (%)	72-hr. acetone extract (%)	Isopentane extract (%)	Isopentane extraction (hr.)	Acetone extract free sulfur (%)	Sodium sulfite free sulfur (2 hr.) %	(6 hr.) %	Total sulfur-acetone extract free sulfur (%)	Acetone-extracted residue sulfur[a] (%)	Isopentane-extracted residue sulfur[a] (%)
1	32% S, pale crepe	3	32.2	26.0	23.0	144	20.0	19.0	19.6	12.2	14.2	15.3
2	32% S, pale crepe	4.5	32.9	9.5	6.6	164	7.4	6.2	7.4	25.2	27.0	27.5
3	32% S, pale crepe	6	33.1	10.9	7.0	310	4.4	2.6	3.5	28.7	30.1	29.6
4	32% S, pale crepe	10	32.7	7.2	2.3	311	1.9	0.6	0.8	30.8	30.5	30.9
5	38% S, pale crepe	10	38.3	7.5	10.0	310	5.3[b]	0.9	1.3	33.0	34.4	35.7
6	45% S, pale crepe	16.5	45.9	17.5	7.1	454	13.1	..	..	32.8	36.2	40.7
7	32% S, GR-S	12	32.0	5.3	0.5	162	..	0.1	0.2	32.0	32.1	31.5

[a] Calculated on extracted residue weight, not on original unextracted sample weight.
[b] Free sulfur by n-hexane extraction was 5.5%.

for different boiling periods.   The implied recommendation of the sodium sulfite method for the free sulfur determination of ebonite made in the A.S.T.M. free sulfur method[6] should be investigated in the light of these results.

There is a discrepancy between combined sulfur calculated on the basis of the difference of the total sulfur and acetone extract free sulfur, and the combined sulfur of the extracted residue.   In each case except that of ebonite 4, a fully cured 32 per cent sulfur ebonite, the former value is lower than the latter even if the extracted nonrubber components are taken into consideration. This disparity is real.   The values given are the means of at least three check results on each sample.   The precision was ±0.1 per cent sulfur in the actual values.   Ebonites 5 and 6, 34.4 and 36.2 per cent sulfur, respectively, are normal hard rubbers, even though they are appreciably above the so-called 32 per cent sulfur limit.
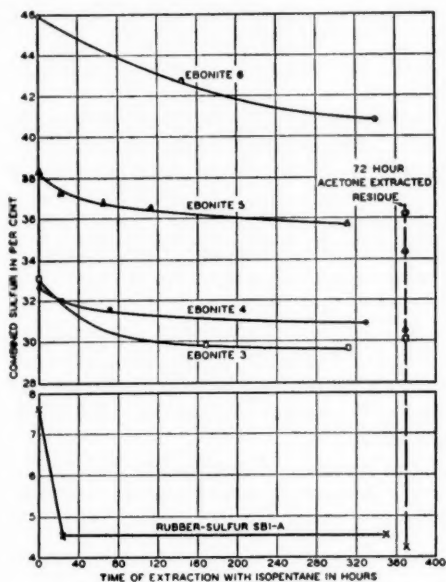
FIG. 3.—Isopentane extraction of ebonites and SB1A.

Methyl iodide reactions were then carried out with two ebonites.   The reaction of methyl iodide with natural rubber ebonite 4 (32 per cent sulfur) is shown in Figure 4.   Extraction of the ebonite with acetone made no appreciable difference in the reaction.   The combined sulfur drops in 800 hours from 30.5 to 20 per cent.   Large quantities of crystalline trimethylsulfonium iodide are liberated from the hard rubber as well as small quantities of iodine.   The shape of this curve is nearly identical with that of the unextracted rubber-sulfur SB1A stock (Figure 1).   About 1 per cent of the iodine is combined in the rubber.

When mercuric iodide is used, a rapid reaction takes place in the first 72 hours, down to 24 per cent sulfur, whereupon only 4 per cent more sulfur is eliminated in the next 900 hours.   Previous acetone extraction has no influence on the reaction.   The hard rubber retains nonextractable mercuric iodide to the extent of 48 to 52 per cent of the final weight of the treated ebonite.   As
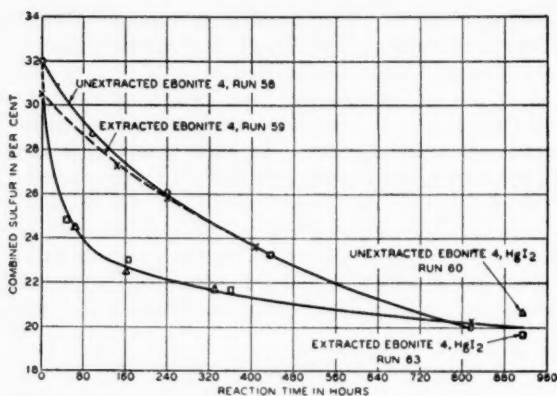
FIG. 4.—Reaction of methyl iodide with extracted and unextracted ebonite 4 at 24° C.

in the soft rubber reactions, the mercury and iodine are in the proportions represented by $HgI_2 \cdot I$. The reaction starts immediately and the hard rubber powder, which normally floats in methyl iodide, sinks to the bottom in 15 minutes. Within a few hours iodine is liberated.

The reaction of extracted GR-S ebonite 7 with methyl iodide is shown in Figure 5. With methyl iodide alone the reaction is directly proportional to time. The rate of removal of sulfur is slower than that obtained with natural rubber ebonite 4 (Figure 4) and shows no inclination to level off. When mercuric iodide is used, the usual rapid reaction takes place and levels out after about 160 hours. The GR-S ebonite 7 dust took 3 hours to settle to the bottom of the flask against 15 minutes for natural rubber ebonite 4. In general, however, the reactions of natural rubber and GR-S ebonites with methyl iodide are very much alike.

No indication of the presence of polysulfide linkages in ebonite is given by the extraction or the methyl iodide experiments. The sulfur elimination curve is hard to interpret because the controlling rate factor is probably the diffusion
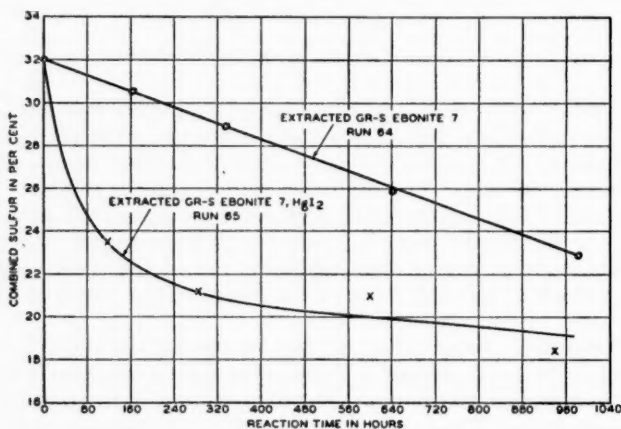
FIG. 5.—Reaction of methyl iodide with GR-S ebonite 7 at 24° C.

through the ebonite, even though 60-mesh ebonite dust was used in all the experiments reported here.

SUMMARY

1. For the soft rubber stock SB1A, there is no evidence for the change: polysulfide → free sulfur on acetone extraction.

2. Evidence for the change: polysulfide → other sulfur links on acetone extraction is indicated by increased reactivity of extracted SB1A to methyl iodide.

3. Natural and GR-S ebonites lose about one-third of their combined sulfur on reaction with methyl idode at 24° C. Trimethylsulfonium iodide is found in large quantities.

4. Neither extraction experiments nor methyl iodide reactions offer evidence for occurrence of polysulfides in 32 per cent sulfur natural ebonite.

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POLYMERIC UNSATURATION AND RELATIVE
RATE OF CROSS-LINKAGE *

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The cross-linking of rubberlike polymers to form networks depends on the presence of chemical unsaturation in the polymer chain when conventional vulcanization reactions with sulfur and accelerator are employed. The rate as well as the extent of cross-linking depends on the concentration of chemical unsaturation per unit chain length. It is the purpose of this paper to deal with the quantitative effect of polymeric unsaturation on the rate of cross-linking rather than to discuss the ultimate mechanism of the vulcanization reaction. Therefore, it is sufficient to consider the regions of chemical unsaturation simply as potential points of cross-linkage.

For this investigation Butyl type polymers offered a unique opportunity to observe the effects of unsaturation, as the amount can be varied several fold. Limitations as to the extent of unsaturation to be studied were dictated by chemical and solubility considerations. The upper limit of the range of unsaturation was sufficiently low so that the sulfur in the system was in excess of that required for complete reactivity. The course of the cross-linking in the vulcanization reaction was followed by volume swelling in a suitable hydrocarbon solvent; therefore, the polymers in the series should possess the same solubility characteristics. These limitations excluded materials that were predominantly polydiolefinic in nature.

General observation of vulcanization of different rubbers has revealed that the higher the unsaturation the faster the rate of cross-linking as measured by a criterion such as extension modulus, but in this present work the author attempted to investigate the course of vulcanization in a more comprehensive manner, especially in the early stages of cross-linking. From the standpoint of practical fabrication of rubber articles, a faster rate of vulcanization commensurate with the properties of the finished goods is very desirable. As another consideration, the balance between polymeric unsaturation and acceleration activity has practical significance. In addition to the quantitative effect of unsaturation on vulcanization rate, observations have been made on the response that two different types of accelerators possess for a series of unsaturations. The differences noted in the behaviors of these two types of accelerators are augmented by data on combined sulfur.

EXPERIMENTAL PROCEDURES

To reduce variables other than polymeric unsaturation to a minimum, the Butyl polymers in these experiments were fractionated to obtain similar molecular weight ranges. Low molecular-weight species decrease the efficiency of cross-linking because they do not enter into a network structure to yield

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a material of recognized physical properties[1].   Preliminary tests were made, and it was shown that low species were extractable after vulcanization.   In addition high molecular species might contribute to a three-dimensional structure by virtue of the entangling probabilities of very long molecules; this has been given as the reason for the gel phase in unmasticated natural rubber[2]. Flory[1] has shown that for a given unsaturation, efficiency of cross-linking is influenced by average molecular weight due to the amount of free end chains which would float in the network.

Fractionation for similar molecular weights.—Six polymers of varying unsaturation were fractionated into four molecular-weight bands in 100-gram lots from 10,000 cc. of C.P. benzene by a method similar to that evolved for polyisobutylene[3].   The precipitation was carried out in a water bath maintained at $25° \pm 0.2°$ C.   The acetone used as the precipitant was first dried over calcium chloride.

Figure 1 is a schematic illustration of the fractionation with the four fractional bands defined by the weight-per cent in the polymer and the incremental
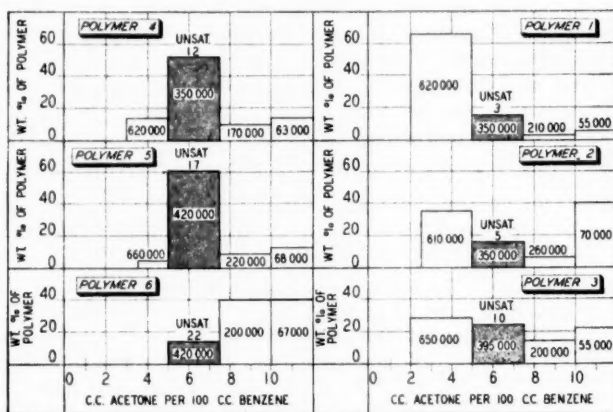
Fig. 1.—Fractionation of Butyls of varying unsaturation.
Shaded cuts used for rate of cross-linking study.

volume of acetone (per 100 cc. of benzene).   Polymer 6 possessed the lowest average molecular weight, and the fractionation was designed to isolate the top 20 per cent of the molecular-weight range.   This range was precipitated between 5 and 7.5 cc. of acetone per 100 cc. of benzene, so the molecular weight band separated by this incremental volume of acetone was selected as the molecular-weight range in which to study the effects of polymeric unsaturation.   The fractions to be used (F 5–7.5) are shown by the shaded rectangles; the viscosity average molecular weight of the various fractional cuts is given for each rectangle; there is reasonable constancy of molecular weight between the respective fractions.

The unsaturations of the fractions F 5–7.5 were determined by the ozonolysis method[4], as it yields more reliable values over a range of unsaturations.   The unsaturation expressed in mole per cent and in molar unsaturation per 1000 monomer units (to eliminate fractional values) are given in Table I, together with the viscosity average molecular weights.

TABLE I

FRACTIONATION OF BUTYLS OF VARYING UNSATURATION

Polymer	Viscosity average molecular weight	Unsstn., mole %	Unsatn. per 1000 monomer units
	Series 1, fraction F 5–7.5		
1	350,000	0.3	3
2	350,000	0.5	5
3	395,000	1.0	10
4	350,000	1.2	12
5	420,000	1.7	17
6	420,000	2.2	22
	Series 2, fraction F 5–7.5		
1	320,000	0.5	5
2	320,000	0.7	7
3	325,000	1.2	12
4	395,000	1.7	17
5	335,000	1.8	18

The second series of fractionated polymers shown in Table I was necessary for the investigation of unsaturation and range of cross-linking when a change in acceleration type was instituted.

Compounding and vulcanization of the fractions.—The first series of fractionated polymers was studied with tetramethylthiuram disulfide as the accelerator, and in the second series, an active thiazole, benzothiazyl-2-monocyclohexyl sulfenamide, was substituted. The unpigmented compounds are as follows:

Series 1	Parts by weight
Polymer fraction F 5–7.5	100
Zinc oxide	5
Sulfur	2
Tetramethylthiuram disulfide	1
Phenyl-β-naphthylamine	0.5

Series 2	
Polymer F 5–7.5	100
Zinc oxide	5
Sulfur	2
Benzothiazyl monocyclohexyl sulfenamide	1.5
Phenyl-β-naphthylamine	0.5

Twenty to 25 grams of each polymer fraction were compounded on a small 6-inch laboratory mill; the ingredients were weighed to the second decimal place as shown. Mixing time was limited to 10 minutes and the roll temperature held near 100° F. Under these conditions a Butyl of 300,000 $\bar{M}_v$ (viscosity average molecular weight) would experience a drop of approximately 10,000 $\bar{M}_v$ units.

To enlarge the curing time differences between these polymers of varying unsaturation, the compounded fractions were vulcanized at a steam temperature of 265° F. Actual rubber temperatures as registered by a mercury thermometer which was inserted in a special well in the mold indicated a temperature of 261° F—a 4° drop from the steam temperature. Temperatures were controlled within ±1.0° F by a recording regulator. In timing the vulcanization reaction, allowance was made for a 12-second rise and fall of the platens of the press. Six to ten points for each polymer of a given unsaturation were obtained to define the course of the cross-linking process.

After vulcanization the thin slabs were extracted in Soxhlet extractors with methylethyl ketone[6]. Ten to sixteen hours were sufficient to remove extractable materials as uncombined sulfur, phenyl-β-naphthylamine, and remnants of accelerator. After extraction the samples were dried in a vacuum oven at 70° C for 2 hours.
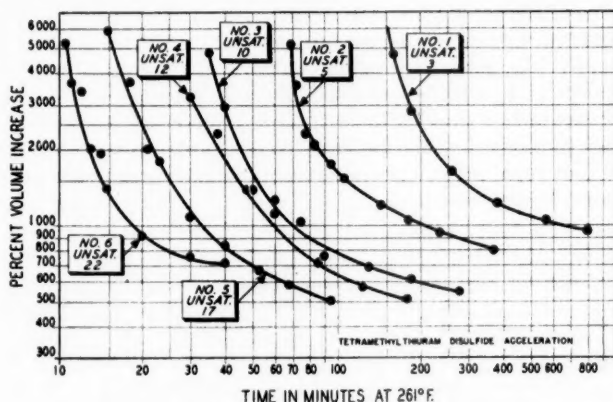
FIG. 2.—Volume swell, in cyclohexane at 25° C, with respect to vulcanization time.

Determination of relative concentration of cross-links.—The initial stages of cross-linkage may lead to insolubility, but these networks do not exhibit tensile properties capable of significant measurement. Therefore, the relative concentration of cross-links over the entire course of reaction can be more readily indicated by equilibrium swell in a suitable solvent.
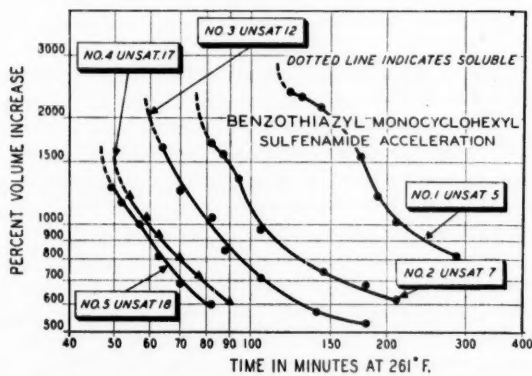
FIG. 3.—Swell of Butyl vulcanizates from fractions F 5–7.5.

Equilibrium swelling in cyclohexane.—The volume swelling is expressed as per cent volume increase and related to the length of time of the cross-linking reaction for the F 5–7.5 fractions by the curves of Figures 2, 3, and 4. The experimental points were determined on two samples ranging in original weight from 0.15 to 0.25 gram. Check determinations were required within 5 per cent, but in most cases the precision was in the neighborhood of 2 or 3 per cent.

Volume increase was determined by measuring the increase in weight of the swollen gel due to imbibition of cyclohexane. Weighing was carried out in glass-stoppered weighing bottles, and the extremely swollen gels were transferred to the bottles with the aid of a wire screen device. The actual swelling in cyclohexane was conducted in a water bath held at $25° \pm 0.2°$ C for 72 hours (in excess of the time required for equilibrium at this temperature).

The curves of Figure 2, for the thiuram accelerator, appear to be almost concentric in nature with the amount of unsaturation establishing the relative position of each; the generally regular pattern of the curves is somewhat disturbed by polymer 6, which had the highest unsaturation. At high concentrations of cross-links—that is, lowest volume increase—the curve appears to divert toward polymer 5; this indicates a premature reversion. However, if comparisons between polymeric unsaturations are made above this point, this factor may be neglected.
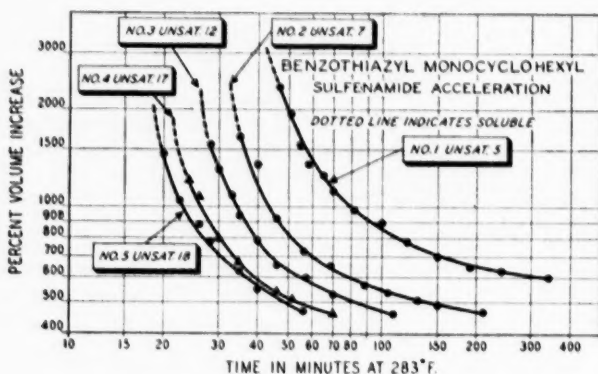
Fig. 4.—Swell of Butyl vulcanizates from fractions F 5–7.

The volume increase time of vulcanization relations for benzothiazyl monocyclohexyl sulfenamide accelerator are given in Figure 3. A concentric pattern is again evident, but the curves exhibit a different behavior from those of Figure 2. In Figure 2, the curves extend from 1000 per cent volume increase towards an extremely low concentration of cross links indicated by 5000 per cent volume increase. In Figure 3, however, the curves are terminated in a time ordinate marked soluble; this means that after only a slight decrease in vulcanization time from the first experimental point, it was no longer possible to obtain an insoluble network. This inability to obtain the very low concentrations of cross-links (found possible with the thiuram acceleration) appears as a characteristic of this active thiazole because the behavior was duplicated at the higher temperature level of 283° F as shown in Figure 4. Compounds accelerated with benzothiazyl monocyclohexyl sulfenamide are characterized by longer induction periods followed by a rapid initial cross-linking.

Perhaps these three series of curves point toward an objective in acceleration research. If the induction periods for this type of thiazole acceleration could be reduced—so that the curves of Figures 3 and 4 would be shifted to the left while maintaining the absence of initial detectable cross-linking—a rapid yet less scorchy vulcanization agent than the thiuram and dithiocarbamates might result.

Relation of concentration of cross-links to extension modulus.—According to Flory and Rehner[6] the volume swelling in a solvent is related to the cross-links between polymer chains. In a simplified form, this theory states that the concentration of cross-links is proportional to the 5/3 power of the volume fraction of polymer in the swollen gel where the volume fraction of the polymer is small. Per cent volume increase is related to volume fraction of polymer by the simple relation:

$$v_2 \text{ (volume fraction)} = \frac{100}{100 + \%} \text{ volume increase}$$

and then:

$v_2{}^{5/3}$ α concentration of cross-links provided (v_2) is small or the per cent volume increase is large.

Before converting the percentage volume increase data of Figures 2, 3, and 4 to a relative cross-linked index, the direct relation of extension modulus to volume swell is shown, as extension modulus is a more familiar criterion of the state of vulcanization (concentration of cross-links). The relation between extension modulus and volume swelling is independent of accelerator type and polymeric unsaturation. As shown in Figure 5, experimental points for ex-
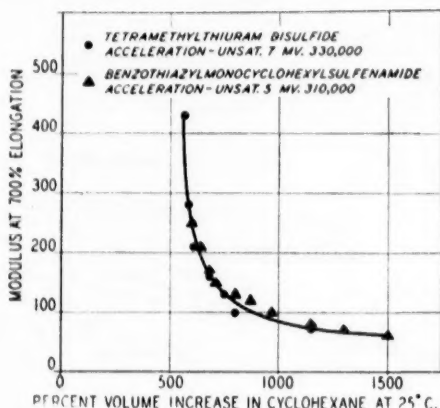
FIG. 5.—Independence of volume swell-extension modulus relation from accelerator type.

tension modulus–volume swell correlation lie on the same curve when two different types of accelerators are used in different unsaturated polymers. In Table II, a special series of volume swelling data is converted to a relative cross-linked index, and corresponding experimental extension moduli at various elongations are compared with these values. In Figure 6, the linear or direct relation of extension modulus and calculated relative cross-links is shown up to the point where crystallization begins to take place. To maintain whole numbers for the range of cross-link concentration, the index is arbitrarily chosen as 1000 times the 5/3 power of the volume fraction of polymer in the swollen gel. From these relations at various elongations, it can be seen that the higher concentrations of cross-links exhibit crystallization at lower elongations. This was shown earlier[7] in these laboratories by the direct observation of x-ray diffractions of stretched vulcanizates, and later by Flory[1] on a basis of stress-strain curves for various Butyl polymers. Therefore, if the times of reaction

TABLE II

CONVERSION OF VOLUME SWELL TO RELATIVE CROSS-LINKS
AND COMPARISON WITH EXTENSION MODULUS

% volume increase in cyclohexane at 25° C	Volume fraction, V_2 in swollen gel $= \dfrac{100}{\% \ V.I. + 100}$	Relative cross-links $= V_2^{5/3} \times 1000$	Extension modulus (lb. per sq. in. at elongation of)		
			600%	700%	800%
1950	0.0488	7.52	40	45	58
1503	0.0624	9.82	46	52	64
1300	0.0714	12.10	54	62	76
1150	0.0800	14.86	75	80	88
970	0.0935	19.23	82	95	118
880	0.1020	23.05	94	114	138
800	0.1112	25.77	108	132	164
710	0.1234	30.62	118	149	208
670	0.1298	33.27	130	170	235
640	0.1350	35.56	152	213	318
610	0.1406	38.02	170	244	378

for the various degrees of unsaturation are determined graphically at 1000 per cent volume increase (18.2 r.c.l.), then comparisons will be made well within the region where the concentration of cross-links and extension modulus are linearly related.
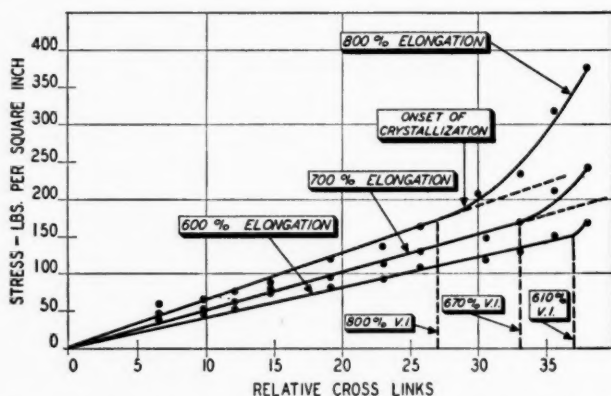
FIG. 6.—Relation of extension modulus to relative cross-links obtained from swelling volumes in cyclohexane.

POLYMERIC UNSATURATION AND CROSS-LINKING

When the experimental volume increase values of Figures 2, 3, and 4 are converted to relative cross-linked index, curves almost the reverse of the volume swelling relations appear. The extent of reaction with time, in Figures 7, 8, and 9, is followed by the cross-link index which has been shown to be directly related to extension modulus.

Variation of rate of cross-link formation with time.—If the curves of Figure 7 are graphically differentiated with respect to time, the rate of increase of relative cross-links passes through a sharp maximum for all but the very lowest unsaturated polymer. This is illustrated in Table III and Figure 10. The rise in reaction rate in the early stages may be consistent with a consecutive type of reaction wherein the final concentration of cross links would depend on the formation of an intermediate product. Such a reaction may be written
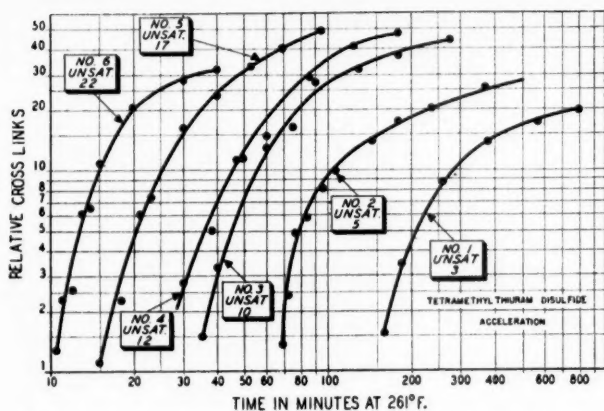
Fig. 7.—Relative cross-links formed with respect to vulcanization time.
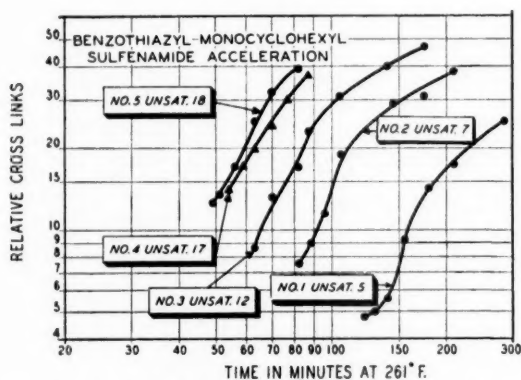
Fig. 8.—Relative cross-links formed with respect to vulcanization time for F 5–7.5 fractions of Butyl polymers.
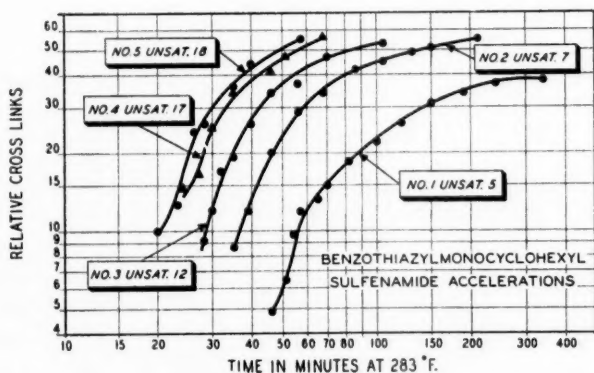
Fig. 9.—Relative cross-links formed with respect to vulcanization time for F 5–7.5 fractions of Butyl polymers.

TABLE III
GRAPHICAL DIFFERENTIATION

t(Time at 261° F)	L(Relative cross-links)	Δt	ΔL	$\Delta L/\Delta t$
Polymer 1 unsatn. 3				
160	1.55			
		20	1.65	0.083
180	3.2			
		20	1.55	0.075
200	4.7			
		20	1.4	0.070
220	6.1			
		20	1.3	0.065
240	7.4			
		20	1.3	0.065
260	8.7			
		20	1.1	0.055
280	9.8			
		20	1.0	0.050
300	10.8			
		50	2.0	0.040
350	12.8			
		50	1.4	0.028
400	14.2			
		50	1.2	0.020
450	15.4			
		50	0.9	0.018
500	16.3			
		100	1.3	0.013
600	17.6			
		100	1.0	0.010
700	18.6			
		100	0.8	0.008
800	19.4			
Polymer 2 unsatn. 5				
69	1.4			
		1	0.3	0.30
70	1.7			
		2	0.7	0.35
72	2.4			
		2	0.8	0.40
74	3.2			
		2	0.9	0.45
76	4.1			
		2	0.8	0.40
78	4.9			
		2	0.5	0.25
80	5.4			
		2	0.4	0.20
82	5.8			
		2	0.5	0.25
84	6.3			
		4	0.7	0.16
88	7.0			
		4	0.7	0.17
92	7.7			
		4	0.7	0.17
96	8.3			
		4	1.4	0.17
100	9.0			
		10	1.2	0.14
110	10.4			
		10	1.1	0.12
120	11.6			
		10	1.0	0.11
130	12.7			
		10	1.1	0.10
140	13.7			
		10	1.7	0.11
150	14.8			
		20	2.2	0.09
170	16.5			
		30	1.5	0.07
200	18.7			

t(Time at 261° F)	L(Relative cross-links)	Δt	ΔL	$\Delta L/\Delta t$
Polymer 3 unsatn. 10				
35	1.5			
		2	0.6	0.3
37	2.1			
		2	0.8	0.4
39	2.9			
		2	0.8	0.4
41	3.7			
		2	0.9	0.45
43	4.6			
		2	0.9	0.45
45	5.5			
		5	2.2	0.44
50	7.7			
		5	2.0	0.40
55	9.7			
		5	1.9	0.40
60	11.6			
		10	3.9	0.39
70	15.5			
		10	3.5	0.35
80	19.0			
		10	3.1	0.31
90	22.1			
		10	2.5	0.25
100	24.6			
		20	4.2	0.21
120	28.8			
		30	4.5	0.15
150	33.3			
		50	5.5	0.11
200	38.8			
		50	3.9	0.08
250	42.7			
		50	2.9	0.06
300	45.6			
Polymer 4 unsatn. 12				
29	2.0			
		1	0.35	0.35
30	2.4			
		2	0.70	0.35
32	3.1			
		2	0.85	0.43
34	3.9			
		2	0.85	0.43
36	4.8			
		2	0.95	0.48
38	5.7			
		2	1.00	0.50
40	6.7			
		2.5	1.35	0.54
42.5	8.1			
		2.5	1.40	0.56
45	9.5			
		5	2.7	0.54
50	12.1			
		5	2.7	0.54
55	14.8			
		5	2.5	0.53
60	17.3			
		5	2.7	0.54
65	20.0			
		5	2.5	0.50
70	22.5			
		10	4.5	0.45
80	27.0			
		10	4.0	0.40
90	31.0			
		10	3.4	0.34
100	34.4			
		20	5.4	0.27
120	39.8			
		20	4.2	0.21
140	44.0			
		40	4.0	0.10
180	48.0			

TABLE III—*Continued*

ΔL/Δt	t(Time at 261°F)	L(Relative cross-links)	Δt	ΔL	ΔL/Δt	(Time at 261°F)	L(Relative cross-links)	Δt	ΔL	ΔL/Δt
	Polymer 5 unsatn. 17					Polymer 6 unsatn. 22				
	15	1.05				10.5	1.28			
0.3			1	0.38	0.38			0.5	0.62	1.24
	16	1.43				11.0	1.90			
0.4			1	0.49	0.49			0.5	0.70	1.40
	17	1.92				11.5	2.60			
0.4			1	0.64	0.64			0.5	0.85	1.70
	18	2.56				12.0	3.45			
0.45			2	1.79	0.89			1	2.15	2.15
	20	4.35				13.0	5.60			
0.45			2.5	2.75	0.10			1	2.40	2.40
	22.5	7.1				14.0	8.00			
0.44			2.5	2.8	1.12			1	2.05	2.05
	25.0	9.9				15.0	10.05			
0.40			2.5	2.7	1.08			2.5	5.70	2.28
	27.5	12.6				17.5	15.75			
0.40			2.5	2.6	1.04			2.5	4.75	1.90
	30	15.2				20.0	20.5			
0.39			5	5.0	1.0			2.5	2.5	1.0
	35	20.2				22.5	23.0			
0.35			5	4.6	0.92			2.5	2.1	0.85
	40	24.8				25.0	25.1			
0.31			10	7.7	0.77			2.5	1.6	0.64
	50	32.5				27.5	26.7			
25			10	5.4	0.53			2.5	1.1	0.44
	60	37.9				30	27.8			
21			10	4.1	0.41			5	1.7	0.34
	70	42.0				35	29.5			
15			20	6.0	0.30			5	1.5	0.30
	90	48.0				40	31.0			

FIG. 10.—Differential curves.
Variation of rate of increase of relative cross-links during course of vulcanization.

hypothetically as:

$$A \longrightarrow B \longrightarrow C$$

where cross-link C depends on the formation of B, and where B may be conceived as a polymer radical or as some activated form for the vulcanization agents.

$$\text{Polymer} + S_8 \longrightarrow \underset{\text{(radical)}}{\text{Polymer-S-}} \longrightarrow \underset{\text{(cross-link)}}{\text{Polymer S S Polymer}}$$

$$\text{Polymer} \xrightarrow{\text{less H}} \underset{\text{(radical)}}{\text{Polymer-}} \longrightarrow \underset{\text{(cross-link)}}{\text{Polymer-Polymer}}$$

$$\text{Polymer} + S_8 \xrightarrow{\text{less H}} \underset{\text{(radical)}}{\text{Polymer--}} + S_8 \longrightarrow \underset{\text{(cross-link)}}{\text{Polymer-}S_x\text{-Polymer}}$$
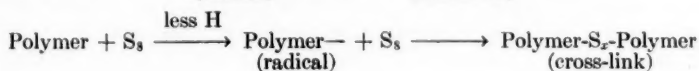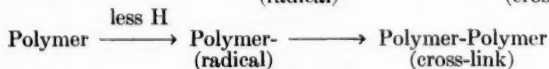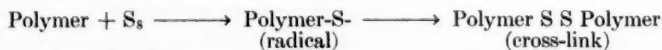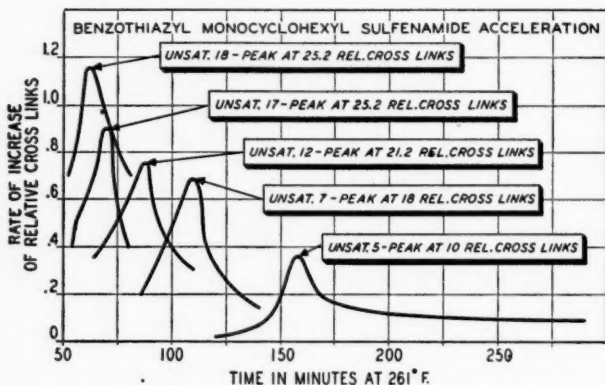
Fig. 11.—Differential curves of Figure 8.
Variation of rate of increase of relative cross-links during course of vulcanization.

These concepts of a consecutive reaction are purely speculative in nature, but are presented in connection with the observation that the rate of cross-linking appears to pass through a maximum.

A similar set of differential curves are obtained by graphically differentiating the curves of Figure 8 for the benzothiazyl monocyclohexyl sulfenamide acceleration. In Figure 11, the differential curves for this type of acceleration show that the course of reaction, after the induction period, is characterized by a sharp rise and an equally sharp descent which passes through a peak near 800 per cent volume increase for the higher unsaturated polymers and near 1500 per cent volume increase for the lower unsaturated fractions. These curves, too, are consistent with the speculative consecutive type of reaction, and as expected, the maximum rate of increase of cross-links descends with decreasing polymeric unsaturation.

Although tetramethylthiuram disulfide and benzothiazyl monocyclohexyl sulfenamide exhibit similar behaviors as regards this consecutive reaction concept, there are some differences as shown in Figure 12, where the progress of the reaction for the two types of accelerators is compared with the progress
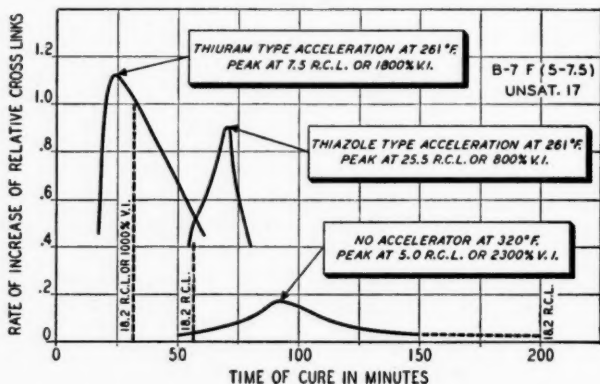
Fig. 12.—Effect of accelerator on rate and course of formation
of relative cross-links.

of reaction where no accelerator is present.   In this series of curves comparisons are made with fractions of similar molecular weight and equal unsaturation.   The thiuram accelerated reaction is characterized by the sharpest rise
to the peak reaction rate, which occurs at a lower state of cure than in the
reaction accelerated by the thiazole where the peak rate occurs at around
800 per cent volume increase or 25.5 r.c.l.   At the constant cure state of 1000
per cent volume increase or 18.2 r.c.l. (where cure time–unsaturation relations
are to be compared) the rate at this point for the thiuram acceleration occurs
on the descending portion of the rate curve whereas the rate with the thiazole
falls on the ascending portion of its respective rate curve.   Therefore inherent
differences exist in the catalytic activity of the two accelerators.   That both
these accelerators are catalysts in the sense of increasing the rate of reaction
can be noted when their rate curves are compared to the one where no accelerator is used.   Further, the nonaccelerated reaction was carried out at 320° F
(so that some reasonable duration of experimental times could be obtained),
whereas the accelerated reactions were carried out at 261° F.   The maximum
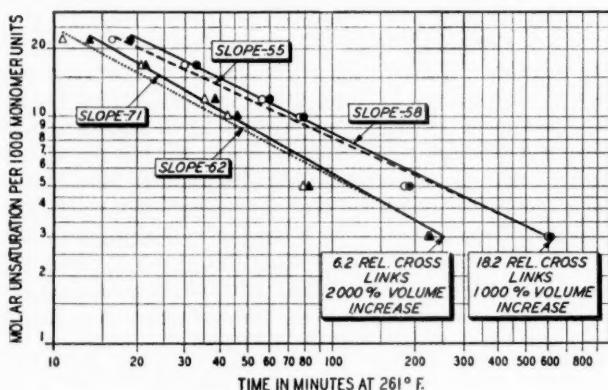
FIG. 13.—Relation of polymeric unsaturation to vulcanization time for
given concentrations of cross-links.

reaction rate obtained with benzothiazyl monocyclohexyl sulfenamide was
almost as high as that obtained with tetramethylthiuram disulfide; it is the
longer induction period which makes the former accelerator a slower curing
catalyst.

Unsaturation and time to constant concentration of cross-links.—In practice,
rate of vulcanization is considered as the time required to obtain a given concentration of cross-links (state of cure) at a given temperature.   In comparing
the effect of unsaturation on the time of vulcanization among the polymers of
varying unsaturation, low concentrations of cross-links were selected.   Figure 6
showed that 1000 per cent volume increase or 18.2 r.c.l. was well within the
region where extension modulus and relative cross links were directly related.
Two thousand per cent volume increase or 6.2 r.c.l. represents a state of vulcanization where recognizable physical properties just begin to appear.

Tetramethylthiuram disulfide acceleration.—Figure 13 shows the effect of
polymeric unsaturation on the time required to reach two different concentrations of cross-links.   The experimental points were taken from either the curves
of Figure 2 at 1000 per cent volume increase or those of Figure 7 at 18.2 r.c.l.
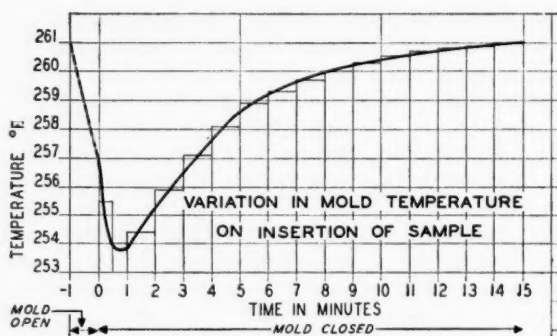
TEMPERATURE °F

FIG. 14.

Aside from one point (slightly below the general relation) the points describe a straight line on logarithmic coördinates with a slope of -0.58. Slope -0.55 is a corrected relationship after time-temperature adjustments were made because the area of the mold about the cavities cooled down when the press was opened to insert the samples for vulcanization. The temperature variation indicated by the mercury thermometer inserted just below the mold cavity followed the cycle shown in Figure 14. This dip in temperature naturally reduced the average temperature, especially for the shorter reaction times. The corrected experimental points (Figure 13) were obtained by determining the average temperature over the designated time, and adjusting the time to a temperature of 261° F by a relation[8] established for Butyl rubber with tetramethylthiuram acceleration. This slope (-0.55) would produce the logarithmic equation, $\log n = -0.55 \log t + c$, which would correspond to an expression $t = c'/n^{1.8}$ on rectangular coördinates where t is the time, n the molar unsaturation, and c a constant depending on the concentration of cross-links.

Benzothiazyl monocyclohexyl sulfenamide acceleration.—In Figure 15, the reaction times to the constant cure state of 1000 per cent volume increase are plotted against the polymeric unsaturation in this thiazole type of accelerated
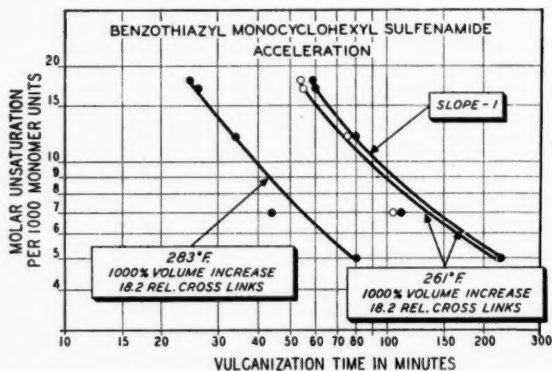
FIG. 15.—Relation of polymeric unsaturation to vulcanization time for a given concentration of cross-links.

compound. This accelerator exhibits a different response to the unsaturation of the polymer than the thiuram previously discussed, as the points (although not quite in a straight line on logarithmic coördinates) yield average slopes close to -1 at both temperatures. The same point at each temperature level lies off the curve; this indicates in all probability a consistent error in unsaturation value of one polymer. This different response to unsaturation yields time-unsaturation relations approximated by an equation, $t = c/n$, which is quite different from the thiuram accelerated compound where t is inversely proportional to the 1.8 power of n.

TABLE IV

COMBINED SULFUR AT CONSTANT STATE OF VULCANIZATION DEFINED BY
1000 PER CENT VOLUME INCREASE OR 18.2 RELATIVE CROSS-LINKS

Tetramethylthiuram disulfide acceleration			Benzothiazyl monocyclohexyl sulfenamide acceleration		
Combined sulfur (%)	Time (minutes)	Unsaturation	Combined sulfur (%)	Time (minutes)	Unsaturation
0.28	22	22	0.42	59	18
0.35	34	17	0.41	61	17
0.35	60	12	0.40	81	12
0.33	80	10	0.40	120	7
0.32	600	3	0.47	230	5

Combined sulfur and acceleration.—The divergent behavior in the response to unsaturation exhibited by the two types of acceleration prompted an investigation into the combined sulfur requirements for the cross-linking of these two series of Butyl polymers. Combined sulfur was determined by the method of Rehner and Holowchak[5] on samples vulcanized for increasing times, and plots were made of time versus combined sulfur. Knowing the times for constant concentration of cross-links from Figures 2 and 3, combined sulfur
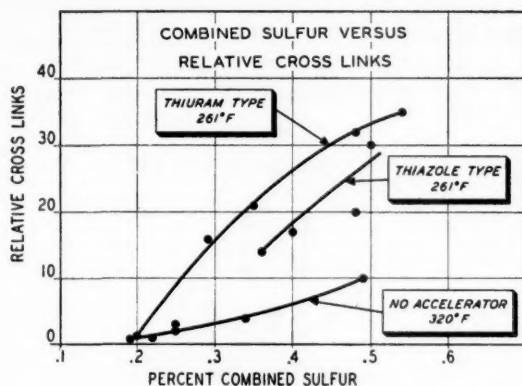
FIG. 16.—Vulcanization of accelerated and nonaccelerated Butyl of unsaturation 17.

values for a constant cure state could be obtained. Such values are given in Table IV and show that, over the range of unsaturations studied, benzothiazyl monocyclohexyl sulfenamide consistently required more combined sulfur for a given cure state than did the tetramethylthiuram disulfide.

This observation suggests that a less potent acceleration would require more combined sulfur for a given concentration of cross-links. Additional

evidence to support this suggestion was obtained by studying the slowest possible cross-linking reaction—namely, a nonaccelerated mixture. Taking the series of three accelerator levels introduced in Figure 12, combined sulfur against state of cure, measured by relative cross-linked index, was plotted (Figure 16) to show that the decreased activity of a nonaccelerated compound requires considerably more combined sulfur for a given state of vulcanization. For example, a 0.4 per cent combined sulfur value yielded a nonaccelerated vulcanizate with a relative cross-linked index of 6.3, whereas the accelerated compounds, for the same combined sulfur, possess over three times the concentration of cross-links.

CROSS-LINKING DIFFERENCES

Empirically, the relation between polymeric unsaturation and reaction time to a given state of vulcanization was represented by the equation $t = c/n^{1.8}$ for the thiuram type of acceleration. When the active thiazole type of accelerator was used, the empirical relation became $t = c/n$. In these equations, t is time, n is the unsaturation per unit chain length, and c is a constant defined by a given cure state. These differences in accelerator response to polymeric unsaturation along with the differences obtained in the combined sulfur requirements can be rationalized by one or more of the following four concepts: the thiuram accelerator may promote a greater number of active centers, for linking, at any one time; the thiuram acceleration may produce a greater number of carbon-carbon linkages; one accelerator might favor more atoms of sulfur in the cross-linked bridge; or there may be a difference in the relative amounts of inter- and intramolecular linkages.

Idealized concepts of possible paths of cross linkage.—Consider two adjacent chains in random motion, both of which may be assigned the same unsaturation per unit chain. If the unsaturation is represented by a line of parallel dots, the number of possible paths of linkage between them can be determined visually by connecting lines as illustrated.

Unsaturation per unit chain	Visual lines of cross-linkage	Number of possible paths of cross-linkage
1		1
2		4
3		9
4		16

The number of possible paths of cross-linkage is equal to the square of the unsaturation per unit chain. Thus, during the initial stages of cross-linking, the rate of reaction should be proportional to the number of possible paths

which has been shown to be equivalent to the square of the unsaturation.   The relation during the initial stages before the formation of a high concentration of cross-links and the subsequent appearance of reversion may be expressed as:

$$\frac{dc}{dt} \propto n^2 \tag{1}$$

where $n =$ molar unsaturation per unit chain and the concentration of cross-links.   The time, then, for a polymer of given unsaturation to reach a constant early state of cross-linkage should be inversely proportional to the square of the molar unsaturation and may be written as:
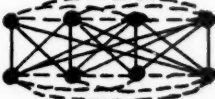
$$t = c/n^2 \tag{2}$$

where the constant, c, is defined by the state of cure or concentration of cross-linkage.

This concept presupposes no intramolecular links which Flory and Rehner[3] state would contribute nothing toward the cross-linked network.   This is reasonable when a few chains are considered, but when a mass of chains is considered, two chains could be disposed so that intramolecular links would be locked in entanglement as shown.
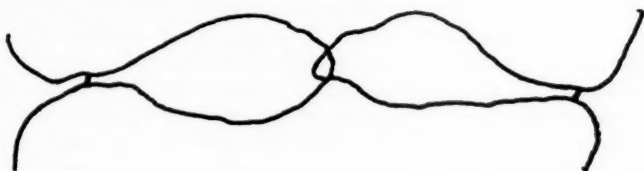
Such a system should have a certain degree of immobility, although efficiency in imparting immobility may not be as great as with the true cross-link. If two adjacent chains are considered as part of a mass of chains and intra-linkages which impart something to the network if properly locked, then the total possible paths of linkage is increased.

Unsaturation per unit chain	Visual lines of total linkage	Number of possible paths of total linkage
1		1
2		6
3		15
4		28

Therefore, if intramolecular linkages are considered as possible network forming bonds, the relation of reaction time to a constant state of cure with polymeric unsaturation should be represented by:

$$t = c/2n^2 - n \qquad (3)$$

Unsaturation would have a still larger influence over reaction time, if this hypothetical relation was valid, for $2n^2 - n$ is always greater than n^2 for values of n greater than 1.

Thus, two hypothetical or ideal relations between vulcanization time and unsaturation are to be compared with the experimentally determined relations. It is evident that the thiuram relation bears a greater similarity to the ideal relation, $t = c/n^2$, where just intermolecular linkages are considered.

Explanations for different accelerator response.—Point one of the four possible explanations for the difference noted in accelerator response raised the question of active centers. The idealized or hypothetical relations of time of vulcanization and unsaturation assumed that all potential points of linkage would be of equal activity if only random motion was assumed. With the work of Farmer[9] and others, it has been well established that, before linking occurs, the polymer chain must itself become a radical through hydrogen acceptance by sulfur or by free radical mechanisms of accelerators. Therefore, it is conceivable that the two accelerators discussed would possess different capacities toward the promotion of active centers for linkage. Thiuram disulfides are well known for their ability to produce free radicals, and thus might transform more of the points of polymeric unsaturation into active centers for linkage. This would explain the fact that an increase in polymeric unsaturation (in these experiments) more effectively increases the relative cure rate with the tetramethylthiuram disulfide than with the benzothiazyl monocyclohexyl sulfenamide.

In connection with the efficiency of producing active centers, some unpublished work from these laboratories[10] reveals differences in thiuram and thiazole behavior that correlate with present observations. In the early work, a Buna-N system was under study, with only 1 part of sulfur based on 100 parts of polymer. In such a system, increasing the quantity of thiuram from 0.1 part resulted in a maximum modulus at about 0.3 part. When a thiazole was used, a maximum modulus, for this sulfur level, was not reached until 5 parts of the thiazole (to 100 parts of Buna-N polymer) had been added. Although in this early work unsaturation was in excess instead of the sulfur, the variations in the accelerator efficiencies were clearly shown.

In the second point, the question of carbon-carbon linkages bears some relation to point one as a free radical mechanism probably would be involved. Thiuram disulfides are known to vulcanize predominantly polydiolefin polymers without additional sulfur, and these vulcanizates possess heat-resistant properties different from a vulcanizate using free sulfur. Therefore, if the thiuram tended to produce some carbon-to-carbon linkages, this type of accelerator would then require less combined sulfur for a given state of vulcanization.
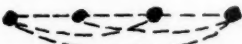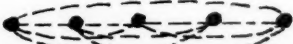
Farmer and Shipley[11] in further work with sulfur and olefins have isolated carbon sulfur bridges of varying sulfur content. In view of the different combined sulfur values reported for a given cross-link concentration when the two different accelerator types were used and, if accelerators have a directing force in this matter, an excess of sulfur for one accelerator would be an insufficiency for another. When conducting these experiments, sulfur was con-

sidered to be in excess of that required for the highest unsaturation when a

$$-\overset{|}{C}-S-S-\overset{|}{C}-$$ bond was assumed.   Perhaps increasing the sulfur dosage

with the thiazole type would make it more responsive to polymeric unsaturation.

Farmer and Shipley also stated that the quality of the vulcanizates might be expected to vary considerably as the proportion of cyclization to cross-linking varied.   They cited the differences between the physical properties and combined sulfur values of accelerated and nonaccelerated rubber vul-

Unsaturation per unit chain	Possible paths of cross-linkage	Visual line of linkage with intramolecular link	No. of possible paths of cross-linkage	Reduction in no. of paths
2	4		0	4
3	9		3	6
4	16		8	8
5	25		15	10

canizates.   As far as combined sulfur against state of cure is concerned, Figure 16 indicates that the thiazole type accelerator is one step removed, from the thiuram behavior, in the direction of a nonaccelerated compound. However, it is rather difficult at this time to see why one accelerator could direct chains to link preferentially in either an inter- or intramanner, for, as far as a segment of a long, randomly placed polymer chain is concerned, it could just as easily link with a segment in its own chain as with one in an adjacent chain.   It would seem that if intralinkages were powerless to contribute anything to the network, a point of diminishing returns with reference to unsaturation could be reached.   For instance, one intramolecular link would reduce the possible paths of cross-linkage as shown by the following series of dots and lines.

Unsaturation per unit chain	Visual lines of intramolecular linkage	No. of possible paths of intramolecular linkage
2		1
3		3
4		6
5		10

In other words, if one intramolecular link occurs in a system of two adjacent chains of n unsaturation, the number of possible paths of cross linkage is reduced by $2n$.

The probability of the occurrence of intramolecular links should increase with increasing polymeric unsaturation. A general expression for such a probability can be worked out by another system of dots representing points of unsaturation in a series of hypothetical polymers.

Let p be the number of possible paths of intramolecular linkage, and is then related to the polymeric unsaturation, n, by the expression:

$$p = \frac{n^2 - n}{2} \qquad (4)$$

It is reasonable to assume then that the actual extent of intramolecular linkages is proportional to the number of possible paths. Thus, the number of

TABLE V

EFFECT OF ASSIGNED PROBABILITY VALUES FOR INTRAMOLECULAR LINKAGE ON UNSATURATION-REACTION TIME RELATION

(When intralinks are assumed to contribute nothing to the network)

k	n	$n^2 - k(n^3 - n^2)$	t	c^a	t
0	5	25	C/25	5500	220
	7	49	C/49		112
	12	144	C/144		38
	17	289	C/289		19
	18	324	C/324		17
0.001	5	24.9	C/24.9	5478	220
	7	48.7	C/48.7		112.5
	12	142.4	C/142.4		38.5
	17	284.4	C/284.4		19.3
	18	318.5	C/318.5		17.2
0.01	5	24	C/24	5280	220
	7	46.1	C/46.1		114.5
	12	128.2	C/128.2		41.2
	17	242.8	C/242.8		21.7
	18	268.9	C/268.9		19.6
0.02	5	23	C/23	5060	220
	7	43.1	C/43.1		117.4
	12	112.3	C/112.3		45.1
	17	196.5	C/196.5		25.8
	18	213.8	C/213.8		23.7
0.04	5	21	C/21	4620	220
	7	37.2	C/37.2		124.2
	12	80.6	C/80.6		57.3
	17	104	C/104		44.4
	18	104	C/104		44.4
0.05	5	20	C/20	4400	220
	7	34.3	C/34.3		128.3
	12	64.8	C/64.8		67.9
	17	57.8	C/57.8		76.1
	18	49.0	C/49.0		89.0

a Adjusted so that curves all start at point $t = 220$; $n = 5$.

actual intralinkages, i, is related to unsaturation by:

$$i = kp = k \frac{(n^2 - n)}{2} \tag{5}$$

It was stated that one intramolecular link reduces the possible paths of cross-linkage by $2n$.   Following such reasoning the original expression relating vulcanization time to polymeric unsaturation, $t = c/n^2$, is modified to become:

$$t = \frac{c}{n^2 - 2nk \frac{(n^2 - n)}{2}} = \frac{c}{n^2 - k(n^3 - n^2)} \tag{6}$$

when intramolecular linkages are considered.

If increasing probability values are assigned to k in Equation 6, as shown in Table V, a series of curves departing from the ideal expression $t = c/n^2$ will be obtained.   Their characteristics are illustrated in Figure 17.   When a
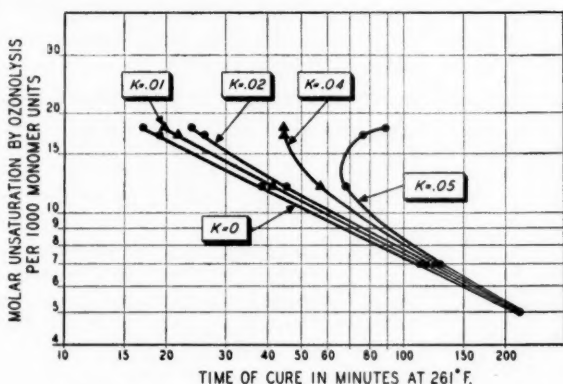
FIG. 17.—Theoretical relation of vulcanization time to polymeric unsaturation at various assigned probability values for intramolecular linkage.

value of about 0.5 has been assigned to k, the curves begin to bend backward as unsaturation reaches the higher levels of this series; this indicates a point of diminishing returns has been reached with reference to polymeric unsaturation. No such phenomenon was observed in this series of experiments, nor has any been reported in the literature.   Two possible conclusions may be drawn from these observations: either the probability of intramolecular links is small within the Butyl ranges of unsaturation or intramolecular links contribute to the cross-linked network.

SUMMARY

In conventional vulcanization reactions with sulfur and accelerator, the rate as well as the extent of cross-linking to form polymer networks depends on the concentration of chemical unsaturation.   The purpose of this paper was to determine the relationships between polymeric unsaturation and the rate of vulcanization.   The course of the cross-linking reaction was followed by volume swelling measurements converted to a relative cross-linked index; this index is shown to be directly related to extension modulus before the onset of

crystallization. Experimental evidence with a system of polymer, zinc oxide, sulfur, and tetramethylthiuram disulfide closely approaches the hypothesis, based on the possible paths of cross-linkage between adjacent chains. The experimental equation, at constant relative cross-links of 18.2 at 1000 per cent volume increase in cyclohexane, is $t = c/n^{1.8}$ when adjustments are applied. When a system utilizing benzothiazyl monocyclohexyl sulfenamide is studied, the time to a constant state of vulcanization is related to the reciprocal of the first power of the unsaturation, $t = c/n$. In both relations, t is time, n is the polymeric unsaturation, and c is a constant which depends on the temperature and state of cure. The difference in response to polymeric unsaturation by these two types of accelerators is reflected in the percentage of combined sulfur for a given concentration of cross-links (state of cure). The thiuram requires less combined sulfur for a given state of vulcanization than does the thiazole, whereas a nonaccelerated mixture requires still more combined sulfur for a given state of cure. In an attempt to rationalize the differences in accelerator behavior, four points are discussed which involve the concepts of active centers, carbon-carbon linkages, varying porportions of sulfur in a carbon-sulfur-carbon bridge, and consideration of inter- and intramolecular linkages.

ACKNOWLEDGMENT

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STRUCTURAL CHANGES IN RUBBER BROUGHT ABOUT BY MOLECULAR OXYGEN

II. KINETICS OF DESTRUCTIVE DISSOLUTION OF VULCANIZED RUBBER *

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In previous communications from our laboratory[1] it was shown that spatial polymers, which are naturally insoluble, are capable of complete solution on being heated in a solvent medium containing molecular oxygen. This dissolution depends on disintegration of the spatial structure of the polymer, which results from disruption of the molecular chains at points where addition of oxygen takes place. It could be foreseen that a similar phenomenon would be observed in the case of vulcanized rubber.

The question as to the behavior of vulcanized rubber with respect to solvents is of considerable interest in explaining the nature of vulcanization. The absence of solubility is one of the characteristics which distinguish vulcanized rubber from crude rubber. Depending on the process mechanism adopted, the loss of ability of rubber to dissolve as a result of vulcanization is explained either as a consequence of the fact that, during vulcanization, the molecular chains of the rubber are integrated by the vulcanization agent into spatial structures, or as a consequence of purely colloid-chemical aggregation processes. In the former case, the molecular chains are linked by main-valence forces; in the latter case, they are linked by intermolecular forces, the intensity of which is increased by the introduction into the molecular chains of the polar groupings contained in the vulcanization agent. The latter hypothesis is advocated by Williams[2] on the basis of his experiments on the dissolution of vulcanized rubber by the action of peptizing agents, such as piperidine, which, by solvating the polar groupings, weaken the intermolecular forces between the individual chains in vulcanized rubber. Williams's experiments, however, were carried out without strict elimination of oxygen, and we were inclined to believe that actually the process observed by this investigator was not peptization of colloidal structures, but rather an oxidative disintegration of the spatial structure of the vulcanizate, similar to the process which occurred in our experiments[3] on the dissolution of the gel fractions of butadiene rubber and of butadiene-styrene rubber.

It seems to us that the experiments described below confirm the correctness of this conclusion.

METHOD AND SUBJECT OF INVESTIGATION

The solution (dispersion) kinetics of vulcanized rubber was investigated with the aid of an apparatus which is sketched in Figure 1.

The apparatus consists of a glass vessel 1, the top of which is connected by means of a ground-glass joint to a condenser 2. To the lower part of the vessel is sealed a tube for feeding oxygen or some other gas, which enters the vessel through the perforated plate 3. The side arm 4, in which a thermometer is fixed by means of a ground-glass joint 5, makes it possible to sample the contents of the vessel. Inside the vessel is suspended a float (shown by the dotted outline), which is a sealed ampoule, on whose surface a layer of the vulcanizate is deposited. The apparatus is immersed to the approximate level of the ground-glass joints in a thermostat filled with petroleum oil, which is equipped with an electric heater and a powerful stirrer. With the aid of a magnetic relay, it is possible to maintain a temperature of 110° C to within ±0.2° C.
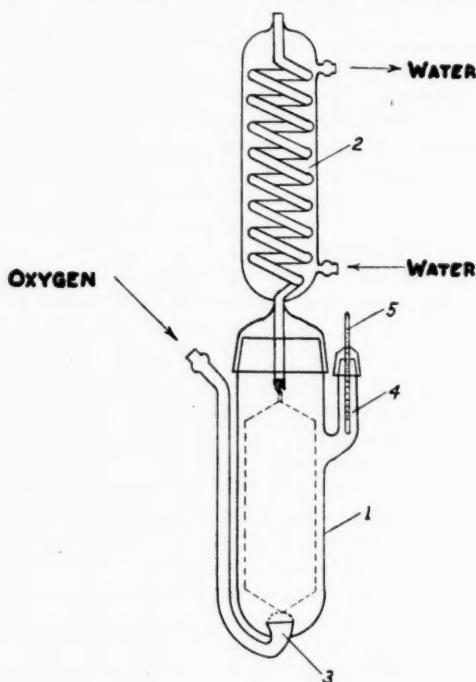
FIG. 1.

The experimental procedure was basically as follows. There was prepared in a mill, by the usual methods, a rubber mixture which consisted of rubber and the ingredients required for vulcanization: sulfur, accelerator, activator. This mixture was then dissolved in nitrogen-saturated benzene; from the solution thus obtained, there was deposited on the surface of the float a coating of the rubber mixture of the desired thickness; the thickness of the coating was controlled by repeated dipping of the float. Following evaporation of the solvent, the float was placed in a vulcanizer—a wide test-tube closed with a rubber stopper, which was provided with a three-way stopcock. The test tube was evacuated, and then filled with carbon dioxide. Evacuation and filling with carbon dioxide were repeated alternately several times to effect complete removal of the solvent, and to remove as much of the occluded oxygen

as possible.   The test-tube, with the float enclosed in it, and with the stopcock open to the atmosphere of carbon dioxide, was then placed in an oil thermostat maintained at a temperature of $141 \pm 0.5°$ C, in which the film was vulcanized. Vulcanization was thus carried out in an inert gas atmosphere; this precluded oxidation and prevented the film from becoming tacky; such tackiness always results when vulcanization is carried out in air.   When optimum vulcanization was reached, the float was withdrawn from the test-tube and cooled in the air. The float was then placed in a specially designed extractor, where the vulcanized film was subjected, in a current of nitrogen and carefully protected from the action of light, to treatment for 16 hours with chloroform cooled down to a definite temperature.   In this manner, a thin film of insoluble vulcanizate remained deposited on the surface of the float.   After being weighed, the float was introduced into the apparatus described above, which was filled with the required quantity of xylene as solvent.   The temperature of the xylene was first adjusted to the desired temperature of the experiment, the solvent being saturated with oxygen or with some other gas, depending on the conditions of the experiment, by bubbling the gas continuously through the perforated plate of the apparatus.   Passage of the gas through the apparatus was continued throughout the experiment.   To prevent the gas current from cooling the reaction space and from entraining any appreciable quantity of solvent while passing through the condenser, the gas was allowed to enter the apparatus only after passing through a wash bottle filled with xylene, which was also placed in the thermostat.   It might be supposed that the gas was equally saturated with the solvent when entering and leaving the reaction vessel.   As a matter of fact, it was shown by control experiments that, when all of the above-mentioned precautions were observed, no more than 1.3 cc. of solvent out of a total of 150 cc. was lost with the exit gas and during sampling over the entire period of the experiment, which was conducted at 120° C.

The process of dissolution was observed by sampling the solution through the side-arm 4.   Since gas was continuously bubbled through the entire mass of solvent during the experiment, the solvent was thoroughly mixed at all times, and the sample represented the average state of the system.   To prevent the solvent from becoming contaminated with particles of vulcanizate mechanically detached from the surface of the film, the float, after weighing the vulcanizate deposited thereon, was inserted in a more or less loose-fitting sack made of fine silk screen, which had been subjected to a preliminary treatment with the solvent.   The presence of the sack did not distort the course of the process. The samples were dried, first in air, and then in a vacuum desiccator at 20° C, to constant weight.   The weighing was done on a microbalance.   The experiments were carried out in duplicate, in two reaction vessels placed in the same thermostat.   As will be seen from the data below, the results showed completely satisfactory checks.

To prepare the vulcanizate, use was made of a mixture which, according to Williams' data[2], corresponded to the least easily peptized product.   The mixture had the following composition:

Rubber (smoked sheet)	100
Sulfur	2
Tetramethylthiuram disulfide	0.2
Zinc oxide	1
Stearic acid	1

Under the particular conditions, optimum vulcanization of this mixture at 140° C was attained in 20 minutes. The vulcanizate possessed the following characteristics:

Chloroform extract	8%
Acetone extract	3.8%
Combined sulfur	1.65%
Tensile strength	190–200 kg. per sq. cm.
Relative elongation	900%

The above results characterize the vulcanizate as being normal for this type of mixture.

EXPERIMENTS ON DISSOLVING VULCANIZATE IN SOLVENT SATURATED WITH INERT GAS AND IN PRESENCE OF PEPTIZING AGENTS

First of all it was necessary to clarify the behavior of the vulcanizate obtained in the above manner by heating in a solvent under conditions which would exclude the destructive action of molecular oxygen previously established by us. With this in view, the vulcanized film, after being extracted with chloroform, was dried at 20° C in a vacuum desiccator which had first been filled with carbon dioxide. The float was then quickly transferred to a dispersion apparatus containing xylene which had been distilled in nitrogen. There was continuously passed through the apparatus a current of nitrogen (from a cylinder), freed from any oxygen contained therein by being passed through a drying and purification train composed of two absorbers which were filled with alkaline pyrogallol solution and an incandescent copper spiral. The vulcanizate was heated for 15 hours at 102.5° C. During this period, no more than 2.8 per cent of the entire weight of the film migrated into the solvent medium. Thus as was to be expected, there could be no doubt that the vulcanizate obtained was insoluble, as well as incapable at the above-mentioned temperature of undergoing any significant thermal disintegration.

The possibility of peptizing the vulcanizate was established in experiments under conditions corresponding to those described in the work of Williams[2]. What fundamentally distinguished our experiments was the fact that molecular oxygen was rigorously excluded, which was apparently not done in Williams' experiments. The procedure comprised the following operations. 0.01-gram samples of extracted vulcanizate, which had been dried in a current of nitrogen in a vacuum desiccator were placed in glass ampoules.

The following materials were introduced into the different ampoules:

(a) 10 cc. of xylene containing 0.2 gram of sodium oleate;

(b) 10 cc. of xylene containing 0.04 gram of piperidine;

(c) 10 cc. of xylene containing 0.04 gram of a condensation product of butyraldehyde with aniline.

Before being sealed, the ampoules were several times alternately evacuated and filled with pure nitrogen. The sealed ampoules were heated for 72 hours at 141° C. No evidence of dissolution of the vulcanizate was observed in any of the ampoules. The lumps of the material swelled, but preserved their configuration and sharp edges. Subsequent storage of the ampoules for approximately one year also failed to bring about any appreciable dissolution of the vulcanizate.

Thus neither the presence in the solvent medium of a surface-active agent (sodium oleate) nor the introduction of the special peptizing agent described by

Williams (piperidine) is capable of bringing about the dissolution (dispersion) of the vulcanizate as long as the medium contains no molecular oxygen.   This fact characterizes the vulcanizate as a system in which the molecular chains are interlinked by main-valence forces; disruption of the latter requires a more intensive agency than the introduction of a peptizing agent.

DISINTEGRATION AND DISSOLUTION OF VULCANIZATE IN PRESENCE OF MOLECULAR OXYGEN.   NATURE OF KINETICS OF PROCESS

An entirely different picture was observed when a vulcanizate was heated in a solvent medium containing molecular oxygen.   In our experiments, this was accomplished by continuous passage of dry oxygen through a solvent contained in the apparatus described above.   In passing through the perforated plate, the oxygen was broken up into fine bubbles, which thoroughly agitated and saturated the solvent.   In this case, the swelling of the film of vulcanizate
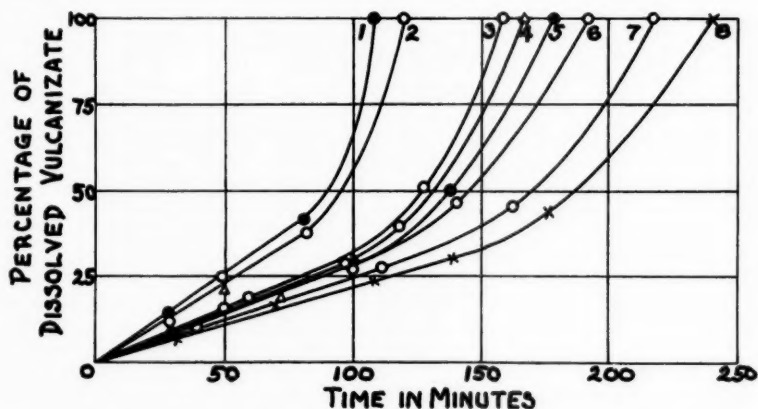
Fig. 2. Solution kinetics of vulcanizate in relative units.   Curves for films of different thicknesses.

1. 0.08 mm.	5. 0.173 mm.
2. 0.109 mm.	6. 0.183 mm.
3. 0.135 mm.	7. 0.205 mm.
4. 0.142 mm.	8. 0.252 mm.

which surrounded the surface of the float was followed by gradual transition of the vulcanizate into the solvent medium, with resulting complete dissolution after 100–250 minutes.

The solution kinetics of the vulcanizate is represented by curves (Figures 2 and 3) which start out in the form of straight lines, corresponding to a time interval until at least 50 per cent of the weight of the vulcanized film is dissolved.   This straightline portion of the curves is the more pronounced the lower the temperature of the process and the thicker the film of vulcanizate deposited on the float.   The straight-line portion of the kinetic curves corresponds to the period during which the reaction rate is constant; this period is followed by an abrupt rise in the reaction rate, which is reflected in the curved portion.   It is not difficult to establish the cause of such a change in the nature of the kinetics by observing the condition of the vulcanized film during the process under investigation.   At the beginning, the film, which has swelled in the solvent, retains its macrosurface intact and adheres firmly to the float; this condition of the film is accompanied by a process which takes place at

constant rate. Thereupon, the film begins to decompose, gradually sliding away from the float, and thus exposing new portions of the surface. This is accompanied by an increase in the rate of the process.

This fact alone is sufficient to show that the reaction does not proceed within the body of the substance, but occurs on the surface, *i.e.*, it exhibits the characteristics of a heterogeneous process. This peculiarity becomes especially pronounced in determining the influence exerted by the dimensions of the film on the kinetics of dissolution of the vulcanizate. The thickness of the vulcanized film was varied by immersing the float a different number of times in the rubber solution. In the individual experiments, the film thickness varied from 0.08 mm. (single immersion) to 0.26 mm. The surface area of the film corresponded to the surface area of the floats, *i.e.*, 69 sq. cm. in one case and 97 sq. cm. in the other.

If the kinetics of the process is expressed in terms of relative values according to the quantity of dissolved vulcanizate as a percentage of the original
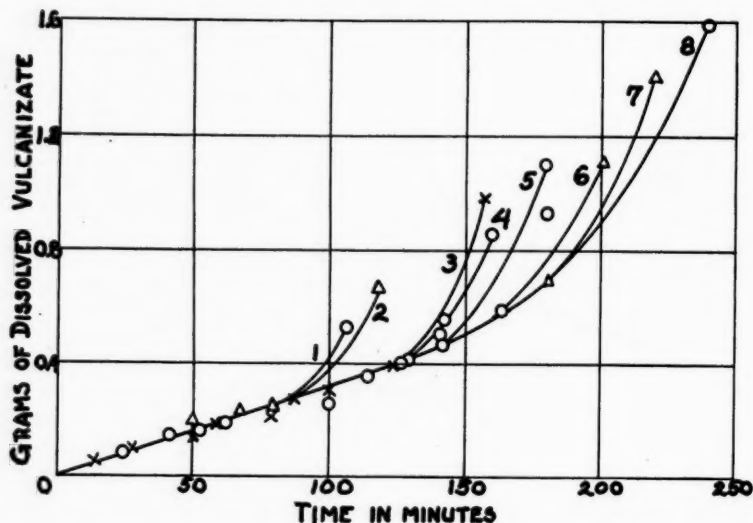
Fig. 3.—Solution kinetics of vulcanizate in absolute units. Curves coded as in Figure 2.

weight of the film, the result is a family of curves arranged in the form of a fan, depending on the film thickness (Figure 2). The thicker the film the lower the relative solution rate of the vulcanizate in the solvent medium. For the rates which characterize the straight-line portions of the kinetic curves, this relationship is expressed by Curve 2 in Figure 4. If, on the other hand, the kinetics of the process is expressed in absolute units, *viz.*, in grams of dissolved vulcanizate, and if the initial surface area of the film is constant, the result is represented by a family of curves whose straight-line portions coincide, regardless of the thickness of the film (Figure 3). The fact that the curved portions are different indicates that, in this part of the process, a change in the effective surface area of the vulcanizate actually does take place, as was suggested above. Thus, the rate of the process, as expressed in terms of absolute units, *e.g.*, in grams per sq. cm. of film surface, is independent of the thickness of the vulcanized film (Curve 1, Figure 4).
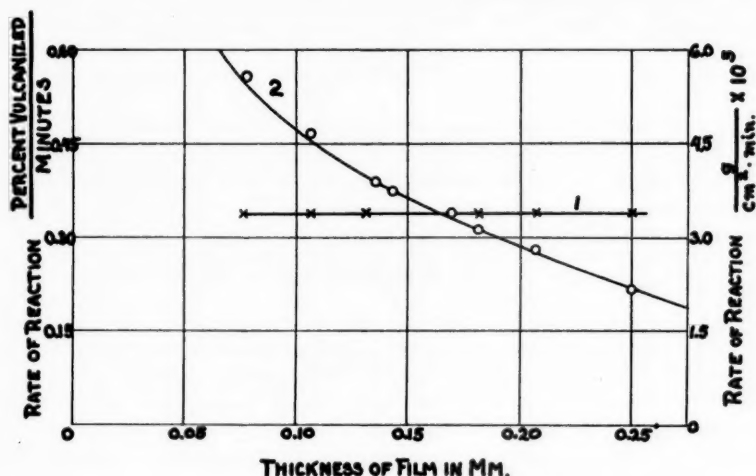
FIG. 4.—Solution rate as function of thickness of vulcanized film.

The experiments described in the present communication definitely point to the fact that the dissolution of vulcanized rubber is connected with the action of molecular oxygen. The transition of the vulcanizate into solution is caused by the breaking away of individual portions of the spatial structure of the vulcanizate as a result of disintegration of the chains at points at which oxygen is added. For this reason, a process of this type may be designated as *destructive solution*.

It might be supposed that the rate of addition of oxygen is lower than the rate of the subsequent chain rupture, and for this reason the overall rate is determined by the former process. If the process is heterogeneous in character, the rate of addition of oxygen to the vulcanizate can be expressed by the following equation:

$$\frac{dO}{d\tau} = k_1 s [O] \tag{1}$$

where s is the surface area of the film, and $[O]$ the concentration of oxygen in the solvent, which is constant because of the conditions under which the experiment is carried out (continuous introduction of gaseous oxygen). The constant k_1 has a composite character, since it also determines the relationship between the concentration of oxygen in the liquid phase and the quantity of oxygen adsorbed on the surface of the film.

On the assumption that the rate of disintegration of the vulcanizate is proportional to the rate of addition of oxygen, we can write:

$$\frac{dKa}{d\tau} = k_2 \frac{dO}{d\tau} = k_1 k_2 s [O] \tag{2}$$

or

$$\frac{dKa}{d\tau} = ks \tag{3}$$

With the aid of the above equation, it is possible to derive a hyperbolic correlation between the relative solution rate (v) and the thickness of the vulcanized film (d).

As a matter of fact:

$$v = \frac{a}{A} = k \frac{sd\delta}{sd_0\delta} \qquad (4)$$

where a is the quantity of vulcanizate dissolved per unit time, A is the initial weight of the film, s is the surface, d_0 is the initial thickness of the film, d is the thickness of the surface layer dissolving per unit time, and δ is the density of the vulcanizate.

On the basis of Equation (4), we have:

$$vd_0 = kd = \text{const.} \qquad (5)$$

The correctness of this equation is confirmed by the data in the third column of Table 1. The thickness d (in the unswollen state) of the surface layer of vulcanizate which dissolves each minute at a partial pressure of oxygen of about 750 mm. and at 102° is $3.5 \cdot 10^{-5}$ cm., which corresponds to $5.9 \cdot 10^{-7}$ cm. per second. This thickness characterizes the linear solution rate, and varies as a function of temperature and partial pressure.

TABLE 1

EFFECT OF THICKNESS OF VULCANIZED FILM ON THE RATE OF
DESTRUCTIVE SOLUTION

Film thickness	Absolute rate g./cm.$^{-2}$ sec.$^{-1} \cdot 10^5$	Relative rate* $\dfrac{d \cdot 100}{b \cdot \tau}$
0.08	3.40	0.516
0.109	3.42	0.44
0.135	3.42	0.37
0.142	3.41	0.35
0.173	3.39	0.32
0.183	3.40	0.29
0.205	3.40	0.25
0.252	3.41	0.22

* In this formula, which expresses the relative solution rate in percentage, d is the weight of vulcanizate dissolved in time τ, and b is the original weight of the film.

EFFECT OF PARTIAL PRESSURE OF OXYGEN ON DESTRUCTION AND SOLUTION RATE OF VULCANIZATE

It follows from Equation (2) that the rate of solution of vulcanized rubber is a function of the concentration of molecular oxygen in the hydrocarbon medium, and consequently a function of the partial pressure of oxygen in the gas phase. To establish this relationship, a mixture of oxygen and nitrogen in different proportions, was passed through the apparatus so that the partial pressure of oxygen in different experiments varied between 756 and 3 mm. Figure 5 shows the results of experiments carried out at 102° C with four different partial pressures. Table 2 shows the numerical rates for the straight-line portions of the kinetic curves; Figure 6 is constructed in accordance with these data. As is seen, when the partial pressure of oxygen changes from 0 to 400 mm., the rate of solution increases substantially linearly with increasing pressure; as the pressure increases from 400 to 756 mm., the rate changes along a parabolic curve; at pressures above 750 mm., the rate changes to an extremely insignificant extent and asymptotically approaches a certain constant value. The above mentioned character of the relationship between the rate of destructive solution of vulcanized rubber and the partial pressure of oxygen
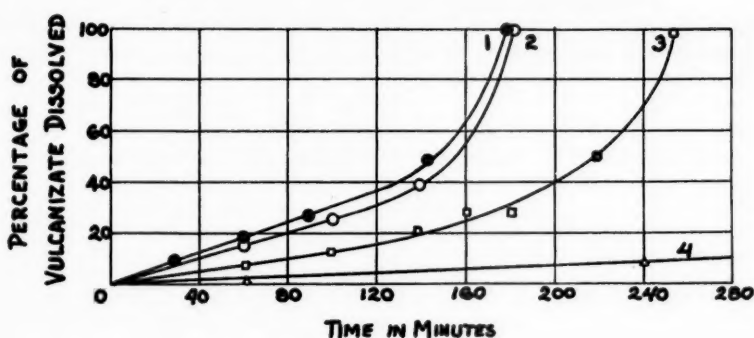
Fig. 5.—Solution kinetics of vulcanizate at different partial pressures of oxygen.

1. 756 mm.		3. 187 mm.	
2. 555 mm.		4. 22.4 mm.	

can be rationalized by starting out with the previously established fact that this process proceeds in the surface layer of the vulcanized film. Our reasoning is similar to that employed by Mark[4] to describe chemical reactions in micellar systems. The rate of fixation of oxygen in a unit of the surface layer may be expressed by the following equation:

$$v_1 = (N_0 - N_t)\alpha\beta P \tag{6}$$

where N_0 is the total number of reaction points in the volume, N_t is the number of points occupied by oxygen, P is the partial pressure, α is a coefficient which determines the solubility of oxygen in xylene, and β is the absorption coefficient.

TABLE 2

RATE OF DESTRUCTIVE SOLUTION OF VULCANIZATE AS FUNCTION OF PARTIAL PRESSURE OF OXYGEN

Oxygen content of mixture (% by vol.)	Barometric pressure (mm.)	Partial pressure (mm.)	Reaction rate g./cm.$^{-2}$ sec.$^{-1}$ $\times$ 10^5
100.0	756.0	756.0	3.44
75.0	739.4	555.0	3.20
53.5	744.0	400.0	2.73
25.0	749.0	187.0	1.65
3.0	746.7	22.4	0.34
0	747.6	0	0.025

The rate of removal of oxygen from the same surface layer constitutes:

$$v_2' = \beta'N_t \tag{7}$$

where β' is a coefficient which defines the proportion of oxygen molecules removed among those present in the surface layer. At equilibrium, $v_1 = v_2$, from which it is possible to determine the value of N_t; the latter is:

$$N_t = \frac{N_0\alpha\beta P}{\alpha\beta P + \beta'} \tag{8}$$

or

$$N_t = \frac{\gamma P}{\gamma P + 1} \tag{9}$$

The dissolution of vulcanized rubber is a result of the disintegration of its molecular chains at the points of addition of oxygen; consequently, this reaction proceeds at a rate proportional to N_t.

Thus

$$\frac{dKa}{d\tau} = kN_t = k'\frac{\gamma P}{\gamma P + 1} \tag{10}$$

where

$$k' = kN_0 \quad \text{and} \quad \gamma = \frac{\alpha\beta}{\beta'}$$

In the case when $\gamma P \ll 1$, Equation (10) assumes the following form:

$$\frac{dKa}{d\tau} = k'\gamma P = k''P \tag{11}$$

In other words, the process of dissolution proceeds at a rate which is proportional to the partial pressure of oxygen. In the case, however, when $\gamma P \gg 1$, Equation (10) assumes the following form:

$$\frac{dKa}{d\tau} = k\frac{\gamma P}{\gamma P} = \text{const.} \tag{12}$$

In other words, the dissolution process proceeds at a constant rate which is not affected by changes in oxygen pressure.
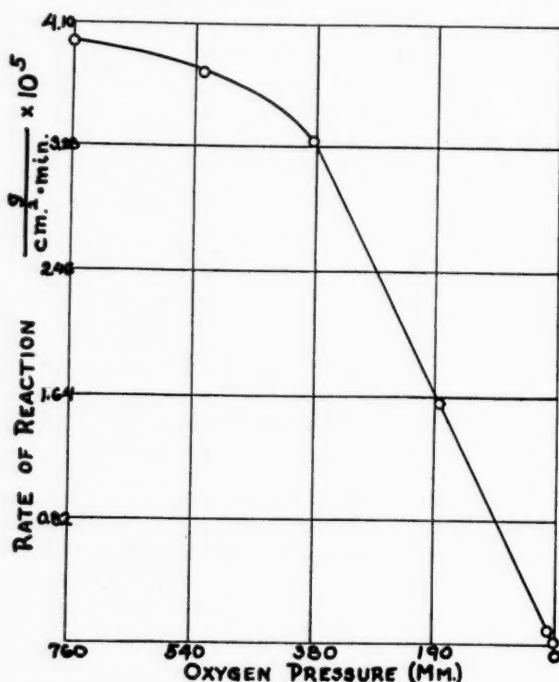
FIG. 6.—Rate of solution of vulcanizate as a function of partial pressure of oxygen.

In our experiments, the former case is realized when the partial pressure changes from 0 to 400 mm. The latter case was not realized completely, although it is evident from Figure 6 that this case corresponds to oxygen pressures above one atmosphere.

EFFECT OF TEMPERATURE ON DESTRUCTION AND SOLUTION KINETICS OF VULCANIZATE

Figure 7 shows the kinetic curves of the solution process for three temperatures: 87.5°, 99°, and 107° C, under a partial pressure of 756–749 mm. To utilize these curves for the purpose of calculating the temperature coefficient and activation energy of the process, it is necessary, in accordance with Equa-
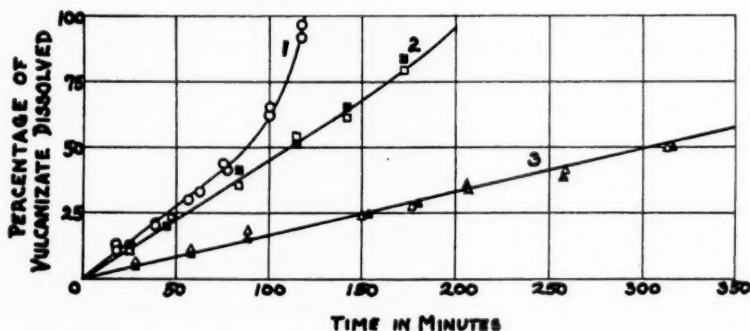
Fig. 7.—Solution kinetics of vulcanizate at different temperatures.
1. 107° C.   2. 99° C.   3. 87.5° C.

tion (2), to know the solubility of oxygen in xylene at the temperatures indicated. We were unable to find any literature data on this subject. However, Williams and Neal[5] did determine the solubility of oxygen in natural rubber within the temperature range indicated above. It may be considered that the temperature dependence of the solubility of oxygen is the same in all hydrocarbon media, for which reason we made use of the data published by these authors to determine the relative change in the solubility of oxygen under our conditions. Table 3 gives the experimentally determined values of the kinetic constants for the straight-line portions of the solution process of vulcanized rubber at the temperatures investigated, as well as the corrected values of these quantities, which were obtained by multiplying the experimental constants by the reciprocal of the relative change in the solubility of oxygen in hydrocarbon media (the solubility of oxygen in rubber at 87.5° C being taken as unity). It should be pointed out that the numerical values of the kinetic constants pre-

TABLE 3

KINETIC CONSTANTS AS FUNCTIONS OF TEMPERATURE

Temperature (° C)	Oxygen solubility (cc. per 100 parts rubber)	Relative oxygen solubility	Experimental constant	Corrected constant
87.5	5.0	1.00	2.17×10^{-5}	2.17×10^{-5}
99.0	3.9	0.78	5.50×10^{-5}	7.0×10^{-5}
107.0	3.0	0.60	6.66×10^{-5}	11.1×10^{-5}

sented in Table 3 differ somewhat from those indicated in Table 2; we are inclined to explain this by a difference in the combined sulfur content of the vulcanization agents employed in the two series of experiments.
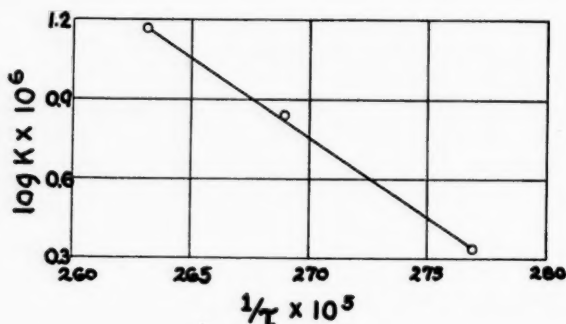
FIG. 8.—Dependence on temperature of the kinetic constants of the dissolution of the vulcanizate.

The corrected values of the constants satisfy the Arrhenius equation (Figure 8). The apparent activation energy of the process, as calculated from these values, is 23,000 cal. per mole. The temperature coefficient of the reaction for the temperature range studied is 2.55.

EFFECT OF PIPERIDINE AND NAPHTHALENETHIOL ON DESTRUCTION AND RATE OF SOLUTION OF THE VULCANIZATE

The experiments described above, in which vulcanized rubber was heated under oxygen-free conditions, showed that, in spite of Williams' data[2], piperidine cannot act as a peptizer for vulcanized rubber. At the outset of our work, we assumed that this investigator, in his experiments, actually carried out a
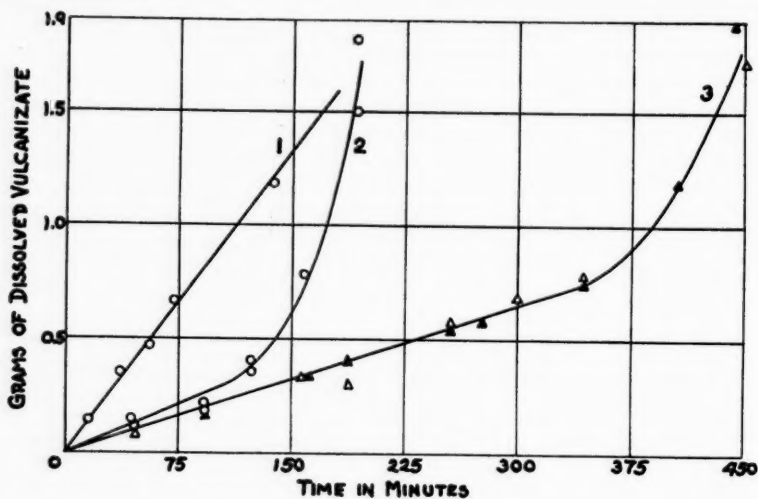
FIG. 9.—Effect of naphthalenethiol and piperidine on the solution kinetics of the vulcanizate.

destructive oxidation of vulcanized rubber, the process being catalyzed by piperidine and the other substances employed by him. To verify this assumption, experiments were carried out in which piperidine was added to the solvent in the amount of 5 per cent of the weight of the rubber. In a way, the results obtained were unexpected from the point of view of Williams' data: the introduction of piperidine leads to a considerable diminution in the rate of solution of the vulcanizate (Figure 9).

The introduction of naphthalenethiol, the use of which is recommended[6] for accelerating the mastication of rubber, and which, according to our data, accelerates the process of rubber oxidation, results in increasing the rate of destruction and dissolution of the vulcanizate (curve in Figure 9).

On the basis of these experiments, it is possible to conclude that the dissolution process of vulcanized rubber is accelerated by substances capable of accelerating the oxidation of rubber (naphthalenethiol), and is retarded by substances which retard the oxidation of rubber. Compounds of the latter type are known to include substances which contain amino groups; it is evident that piperidine, too, can be counted among these substances.

VARIATION OF VISCOSITY OF SOLUTION

The process of disintegration of vulcanized rubber takes place not only on the surface of the film, but continues in the solvent medium as well. This is apparent from the change in viscosity of the solution obtained as a function of the time of treatment of the film. In experiments carried out specifically for this purpose, samples of the solution were diluted to the same concentration of 0.36 per cent, and their viscosities were determined with a Skarp viscometer. The results are shown in Figure 10. As is seen, the viscosity of the solution varies as a function of time of dissolution, and follows a curve whose maximum has a time coördinate which corresponds to an abrupt acceleration of the process. The very fact that the viscosity of these solutions of equal concentration undergoes a change, indicates a change either in the dimensions or in the configu-
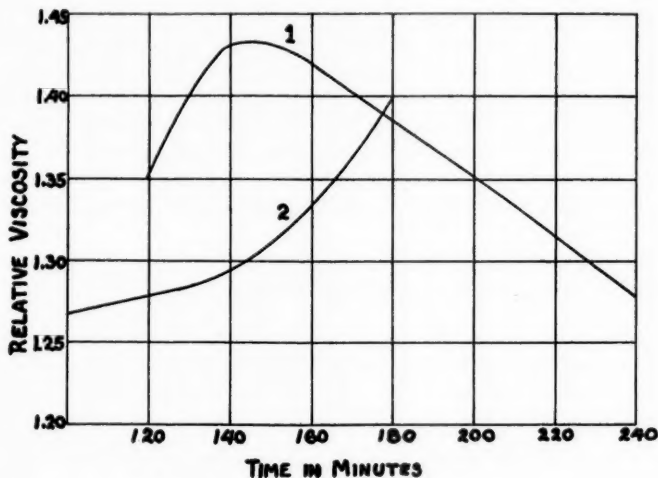
FIG. 10.—Change in viscosity of solution during dispersion (Curve 1). Curve 2 represents the solution kinetics.

ration of the particles of dispersed vulcanizate, *i.e.*, shows that the disintegration process continues in solution. The character of the change described above can, as a first approximation, be explained in the following manner. As a result of the continuing disintegration of the particles of vulcanizate in the xylene medium, the solution contains particles of different sizes: larger particles which have just separated from the film, and smaller particles which have been formed from the former during subsequent stages of disintegration. The viscosity of the solution appears to depend on the size and configuration of these particles. The maximum viscosity is observed precisely when, at the moment of maximum rate of disintegration of the film, the solution contains the highest proportion of large particles.

DISCUSSION OF RESULTS. STRUCTURE OF VULCANIZED RUBBER

It was pointed out in the introduction that the establishment of the conditions under which vulcanized rubber is capable of dissolving would be of considerable importance in connection with determining the character of the structure of vulcanized rubber and the nature of vulcanization. It has been established in our experiments that vulcanized rubber, when carefully protected from atmospheric oxygen, is incapable of going into solution either on being heated to 140° C or on being subjected to the action of peptizers or of polar substances added to the solvent. This serves to confirm the existence of valence bonds between the molecular chains in vulcanized rubber, and agrees with the bridge theory of vulcanization. The transfer of vulcanized rubber into the solvent medium is possible only under the action of factors capable of overcoming main valence forces. This is precisely what takes place during the process of dissolution of vulcanized rubber by the action of molecular oxygen, which is described in the present communication. Both the character of the solution kinetics (in particular the fact that the rate of the process is a function of the partial pressure of oxygen) and the magnitude of the activation energy of the process (which constitutes 23,000 cal. per mole) point to the chemical nature of this process and to the participation of molecular oxygen in it. The disintegration of the molecular chains takes place at the points of addition of oxygen, similar to what is observed during the ozonization of rubber. The true mechanism of this process is not yet clear. The fact that the solution products of vulcanized rubber contain carboxyl groups is an indirect indication of the correctness of the repeatedly stated supposition that this disintegration is connected with a decomposition of peroxide groupings, which are formed on addition of oxygen at the double bonds, either directly or else, according to Farmer[7], as a result of a series of consecutive transformations following on the addition of oxygen.

In our next communication, the results of investigations on the properties of the dissolution product of vulcanized rubber will be presented, and it will be shown that this product contains carboxyl groups, whose average equivalent weight is approximately 8,000. A comparison between the average molecular weight of the disintegration products, as determined by Lamm's method (3,600), with the equivalent weight derived from the acid number (8,000) shows clearly that this disintegration leads not only to the formation of carboxyl groups at the ends of the chains, but also to the formation of other groups as well, in particular carbonyl groups. The entire process involved in the phenomenon described by us follows this scheme: oxidation → disintegration → dissolution. In correspondence with this scheme, we propose to term this process *destructive*

solution, which denotes its chemical nature, and which is not true of the phenomena of ordinary solution.

A study of the properties of the destructive solution product of vulcanized rubber leads to data which are in complete agreement with the scheme indicated above, and which, on the other hand, contradict the statements of Williams[2] and of other authors concerning the possibility of dissolving vulcanized rubber under the action of peptization as a colloid-chemical inversion of the vulcanization process. The product obtained has a relatively low molecular weight; its light-scattering obeys Rayleigh's law; and it obeys Einstein's viscosimetric equation over a wide range of concentrations. The particles of the product possess a mean axial ratio of 24:1, which, in view of their molecular weight of 3,600, characterizes them, by the crudest estimate, as particles consisting of three or four interconnected chains, each of which contains 12 to 15 isopentene groups. Thus, these particles are fragments of the spatial structure which is characteristic of the original vulcanizate.

CONCLUSIONS

1. Under conditions of complete isolation from molecular oxygen, vulcanized rubber is incapable of going into solution either on being heated to 140° C or by the action of surface-active substances and peptizers.

2. Vulcanized rubber dissolves on being heated in a solvent medium (xylene) containing molecular oxygen.

3. A method for studying solution kinetics has been developed which makes it possible to maintain the surface area of the vulcanizate and the partial pressure of oxygen constant. Under these conditions, the process proceeds at a constant rate.

4. The relative rate of solution is a hyperbolic function of the thickness of the vulcanized film. The absolute rate of solution is independent of this factor.

5. The process of dissolution takes place in the surface layer of the vulcanizate, whose thickness determines the rate of linear solution; under a partial pressure of oxygen approximating 760 mm., and at a temperature of 102° C, the rate of linear solution is 5.9×10^{-7} cm. per second.

6. As the partial pressure of oxygen increases up to 400 mm., the rate of solution rises linearly; as the pressure is increased from 400 to 750 mm., the rate of solution rises in conformance with a parabolic function; at pressures above 750 mm., the rate of solution changes only insignificantly while approaching a constant value. The general expression for the above correlation has the following form:

$$v = \frac{k\gamma P}{\gamma P + 1}$$

7. The kinetic constants of the solution process of vulcanized rubber follow Arrhenius's equation. The apparent activation energy equals 23,000 cal. per mole.

8. Piperidine retards the solution process of vulcanized rubber; naphthalenethiol and other oxidation accelerators increase the rate of solution.

9. The solution process is considered to be the result of disintegration of the spatial structure of vulcanized rubber, which takes place as a consequence of oxidation and disintegration of the molecular chains of rubber at the points of addition of oxygen. The entire process follows this scheme:

Oxygen addition → disintegration → dissolution

10. The results obtained are in agreement with the concept of vulcanization as a process in which the most important part is played by the linkage of molecular chains into a unified spatial structure by the action of main-valence forces.

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STRESSES AND BIREFRINGENCE IN RUBBER SUBJECTED TO GENERAL HOMOGENEOUS STRAIN *

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INTRODUCTION

In a previous paper[1] the author dealt with the theory of the optical properties of strained rubber on the basis of a model in which the rubber was envisaged as a network of long-chain molecules of randomly jointed links. These links were assumed to be optically anisotropic, having two different optical polarizabilities, in directions parallel and perpendicular to their length. The theory was applied to the case of the most general homogeneous deformation of rubber, and it was shown that, for each of the three principal directions of strain, there is an associated optical polarizability, by which the refractive index for light having the corresponding direction of electric vector is determined. If λ_1, λ_2 and λ_3 are the principal extension ratios, and n_1, n_2 and n_3 the corresponding refractive indices, the double refraction for light propagated along the direction λ_3 may be represented by the equation:

$$n_1 - n_2 = \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \cdot \frac{2\pi}{45} N(\alpha_1 - \alpha_2) v_r^{\frac{1}{3}} (\lambda_1^2 - \lambda_2^2) \qquad (1)$$

in which $\bar{n}$ is the mean refractive index, N the number of molecular chains per cc., and $\alpha_1 - \alpha_2$ the difference of polarizabilities for the link of the chain. The quantity v_r refers to the volume fraction of rubber in the case when the rubber is swollen in an optically inert solvent. Comparison of this result with the corresponding equation for the difference of principal stresses[1] i.e.:

$$t_1 - t_2 = NkTv_r^{\frac{1}{3}} (\lambda_1^2 - \lambda_2^2) \qquad (2)$$

where t_1, t_2, t_3 are the principal stresses, k is Boltzmann's constant, and T the absolute temperature, leads to a linear relation between the birefringence and the stress-difference, which has already been examined experimentally for the case of a simple elongation in an earlier paper[2].

EXPERIMENTAL METHOD

In the present paper a study of the stresses and birefringence in the most general type of homogeneous strain is reported. For this purpose a sheet of vulcanized rubber, compounded according to the formula given in the paper referred to[2], was stretched in two directions at right angles in such a way that the strain was homogeneous, while the two principal extension ratios λ_1 and λ_2 in the plane of the sheet could be varied independently by the application of

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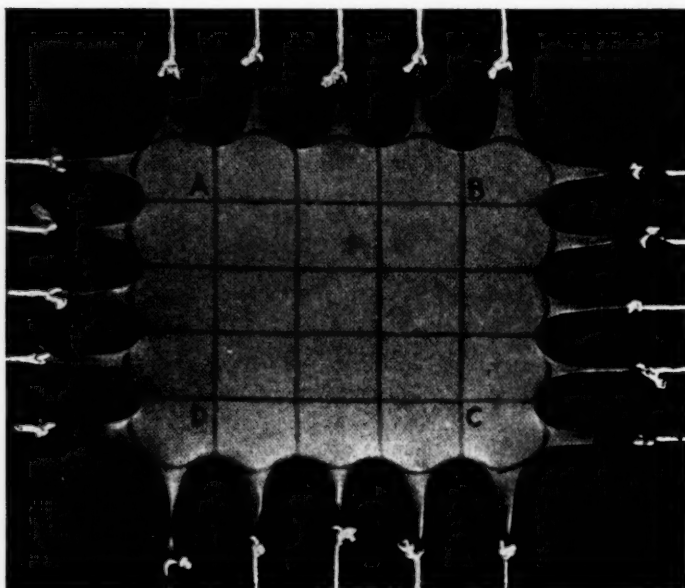
Figure 1.—Rubber sheet stretched by factors of 2·5 and 2·0 in two perpendicular directions.

1 cm.
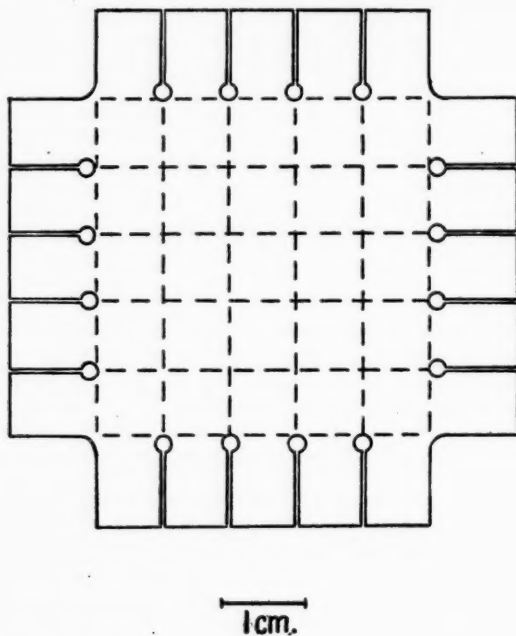
Figure 1 (a).—Form of unstrained sample.

two sets of forces.   The arrangement used permitted the simultaneous measurement of the principal stresses and the double refraction corresponding to any state of strain.

It is not easy to devise a suitable method for applying two unequal strains to rubber in two perpendicular directions.   The method here adopted, though not ideal, particularly in that the maximum attainable strain was limited, seemed to provide the simplest means of achieving the desired result.   It makes use of the principle of the guard plate to eliminate the effect of the nonuniformity of the strain in the vicinity of the edges of the sheet.   The shape of the test-piece is shown in Figure 1.   It was in the form of a square, with five projecting lugs on each side, to which strings were tied for the application of the loads.   The surface of the sheet was marked out with a series of lines forming a square lattice, so that the state of strain at all points could be observed.   With the sheet placed horizontally, the three middle lugs on one side were loaded by means of three equal weights attached to strings passing over pulleys; the strings attached to the two outermost lugs were secured to a rectangular frame, mounted horizontally.   The five strings on the opposite side were connected to the opposite side of the frame.   Similarly, the three middle lugs on an adjacent side carried three equal weights; the two outer lugs, as well as the five on the side opposite to them, were connected to the frame.   The 14 strings connected to the frame were provided with tension adjusters, and these strings, as well as the pulleys, could be moved sideways independently, so that each set of strings could be kept parallel and the two sets maintained perpendicular to each other.   The appearance of the stretched sheet when the tension on the outer lugs was suitably adjusted is shown in Figure 1; in all cases the strain within the rectangle ABCD was sensibly uniform.   Under these conditions it was assumed that the stresses acting on the sides of the rectangle ABCD were defined by the loads applied to the three central lugs, and that the nonuniform edge region, though requiring the use of a slightly different tension on the outer lugs[3], would be without effect on the stress in this inner uniformly strained region.

For the optical measurement, a beam of light from a polarizer set at 45° to the directions of principal strain was passed normally through the sheet, the birefringence being measured by means of a Babinet compensator.

The measurements were made at room temperature, which varied between 17 and 22° C.

EXPERIMENTAL RESULTS

The data obtained are given in Tables 1 and 2.   Table 1 refers to the dry rubber, and Table 2 to the same rubber swollen in medicinal paraffin to $v_r = 0.525$.   Readings were taken in the order given in the tables.   Generally about 10 minutes elapsed between the application of a load and the taking of readings.   The forces f_1 and f_2 are the loads in grams applied to each of the three middle lugs; the areas of cross-section of the rubber in the unstrained state (A_0), over which these forces act are given in the table.   The figures for optical retardation are given in terms of the number of sodium wave lengths phase difference between the two rays, this being the quantity actually measured.   To convert this to difference of refractive indices $(n_1 - n_2)$ it is only necessary to divide by the thickness of the sheet and multiply by the wave length.   The extension ratio λ_3 and the corresponding thickness in the strained state were determined from the measured λ_1 and λ_2, assuming no change of volume on straining.

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TABLE 1

DRY RUBBER.   THICKNESS = 0.082 CM. A_0 = 0.0648 CM².

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f_1 (g.)	f_2 (g.)	λ_1	λ_2	Retardation (sodium wave lengths)
100	100	1.07_0	1.08_3	−0.02
100	200	0.97_8	1.29_7	−0.55
200	200	1.16_7	1.20_9	−0.07
300	200	1.46_0	1.09_1	+0.54
300	100	1.58_2	0.90_5	+1.06
300	300	1.35_0	1.37_0	−0.05
300	400	1.18_3	1.88	−0.80
200	400	0.93_3	2.04	−1.50
100	400	0.78_3	2.14	−2.00
400	400	1.60	1.72_5	−0.13
500	400	2.24	1.51_3	+0.64
500	300	2.42	1.09_6	+1.39
500	200	2.51	0.87_5	+2.05
500	100	2.64	0.72_5	+2.80
500	500	2.07	2.10	−0.05
600	500	2.68	1.87_5	+0.54
400	600	1.25_0	2.98	−1.55
300	600	0.98_0	3.06	−2.31
200	600	0.79_1	3.14	−3.05
100	600	0.67_9	3.21	−3.76
600	600	2.34	2.63	−0.18

In addition to the data in Tables 1 and 2, figures were obtained for the case of simple elongation, *i.e.*, with $f_2 = 0$, using a parallel strip of rubber cut from the same sheet.   These additional data are included in the graphical presentation of the results.

The optical data are presented in Figures 2 and 3, omitting points (near the origin) corresponding to the case when $f_1 = f_2$.   In the first case (Figure 2) the

<div align="center">

TABLE 2

RUBBER SWOLLEN TO v_r = 0.525 IN PARAFFIN.   THICKNESS (SWOLLEN) = 0.099 CM.
A_0 = 0.0985 CM².

</div>

f_1 (g.)	f_2 (g.)	λ_1	λ_2	Retardation (sodium wave lengths)
100	100	1.08_8	1.08_8	−0.02
100	200	0.99_6	1.30_5	−0.40
200	200	1.21_5	1.19_3	+0.01
300	200	1.55	1.06_8	+0.51
300	100	1.66	0.88_2	+0.93
300	300	1.41	1.36_4	+0.03
100	400	0.80	2.04	−1.46
200	400	0.95_6	1.95_3	−1.02
300	400	1.24	1.83	−0.51
400	400	1.65	1.65_4	0.00
400	500	1.50	2.12	−0.46
500	500	1.97	1.94	+0.02
500	300	2.31	1.10	+1.06
500	200	2.43	0.85_8	+1.62
500	100	2.48	0.73_5	+2.07
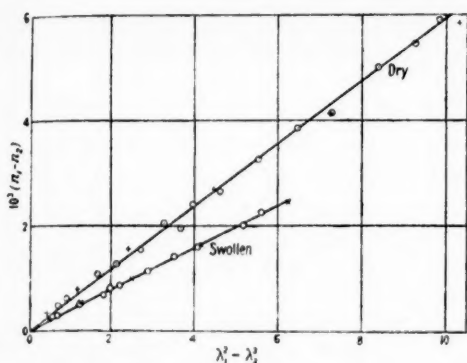
FIG. 2.—Birefringence plotted against difference of squares of principal extension ratios for dry and swollen rubber. The crosses refer to simple elongation.
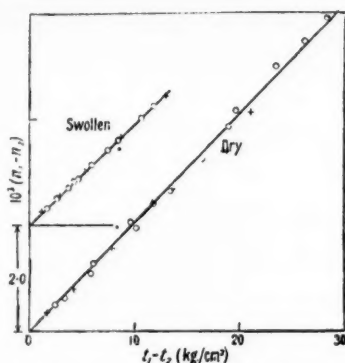
FIG. 3.—Birefringence plotted against difference of principal stresses for dry and swollen rubber. The crosses refer to simple elongation.

birefringence is plotted against the difference of the squares of the corresponding extension ratios, $\lambda_1^2 - \lambda_2^2$. While the expected linear relationship (Equation (1)) is approximately borne out, there are for the dry rubber, slight departures which are probably greater than the errors of measurement. For the swollen rubber, on the other hand, the agreement with the theoretical form is very close. In the second case (Figure 3) the birefringence is plotted against $t_1 - t_2$, the difference of the principal stresses. Again, the proportionality is more exact for the swollen than for the dry rubber.

Figure 4 represents the difference of the two principal stresses, plotted against $\lambda_1^2 - \lambda_2^2$, for both samples. As with the birefringence, the swollen rubber appears to agree with the theoretical form (2) within the experimental error, but the agreement in the case of the dry rubber is not exact.

FURTHER EXAMINATION OF STRESSES

Although the evidence presented in Figures 2, 3 and 4 suggests that the theoretical expectations regarding the dependence of the birefringence and of the principal stress difference on the two principal extensions in the plane of
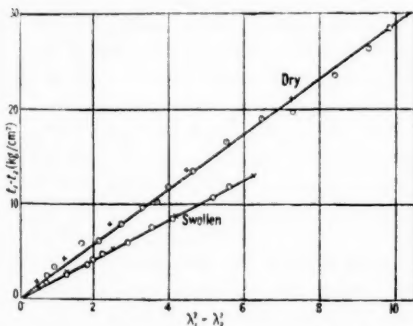
FIG. 4.—Difference of principal stresses plotted against difference of squares of principal extension ratios. The crosses refer to simple elongation.
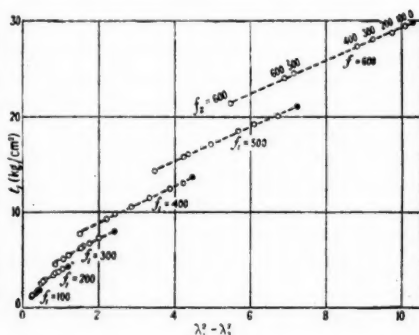
Fig. 5.—Dry rubber. Stress t_1 plotted against $\lambda_1^2 - \lambda_2^2$. The black circles refer to simple elongation. f_1 and f_2 are expressed in grams.

the sheet are approximately fulfilled, particularly in the case of the swollen rubber, an examination of each of the principal stresses separately reveals consistent deviations from the theoretical form, as will now be shown.

Since the stress t_3 normal to the sheet is zero, we should have, according to the theory previously outlined[1]:

$$t_1 = G(\lambda_1{}^2 - \lambda_3{}^2) \tag{2a}$$

with a corresponding expression for t_2. According to this equation, a plot of t_1 or t_2, against $\lambda_1{}^2 - \lambda_3{}^2$ or $\lambda_2{}^2 - \lambda_3{}^2$, respectively, should yield a straight line. The actual results, shown in Figures 5 and 6, present a more complex appearance for both the dry and swollen rubber.

The method of plotting employed in these diagrams requires a little explanation. First it must be remembered that the stress (say t_1) is determined by the force (f_1) divided by the area of cross-section, which is itself a function of the strain, i.e., $t_1 = \lambda_1 f_1/A_0$. Hence, while one of the forces is held constant, the
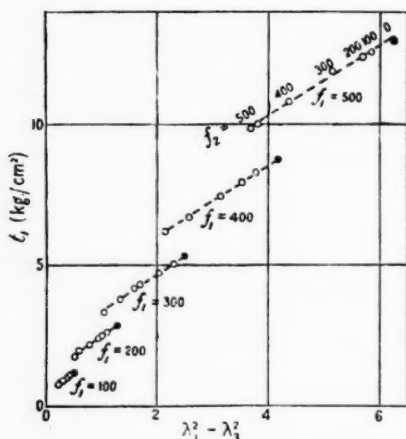
FIG. 6.—Swollen rubber. Stress t_1 plotted against $\lambda_1{}^2 - \lambda_3{}^2$. The black circles refer to simple elongation.
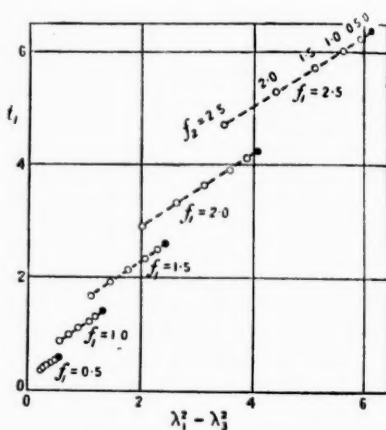
FIG. 7.—Stress calculated from Mooney's equation, using $G = 1.0$, $K = 0.1$.

stress corresponding to this force varies with changes in the second force, since such changes alter all the extension ratios. To simplify the presentation, the stress plotted is referred to as t_1, and the corresponding force as f_1. Thus two points appear on the diagram for each state of strain, one for each of the two principal stresses.

It is seen that the points fall on a set of lines, on any one of which f_1 is constant, while f_2 varies. This clearly means that t_1 is dependent on a more complicated function of the extension ratios λ_1, λ_2 and λ_3 than the one represented by Equation (2).

This important departure from the theoretical form exhibited when the principal stresses are plotted separately is rather surprising in view of the fair agreement obtained when only their difference is considered. Before discussing its significance, it seems desirable to examine very carefully the nature of the evidence to make sure that it is not due to some spurious effect introduced by the experimental technique. Three possible sources of trouble will be dis-

cussed, namely (1) relaxation, (2) anisotropy in the original sheet, and (3) nonuniform strain round the edges.

RELAXATION

It is true that the attainment of equilibrium values of the stresses in strained rubber is a matter of considerable difficulty, requiring the breaking-down of temporary intermolecular cross-links by the use of higher temperatures or other means. No attempt was made to obtain genuine equilibrium values in the present experiments, and it is therefore necessary to consider whether the discontinuous array of Figures 5 and 6 might arise from this cause.

There are two reasons for rejecting this hypothesis. First, although it was observed that the values of the strain parameters obtained under the application of a given pair of forces depended to some extent on the order of application of the forces and on the previous history of the sample, nevertheless, the stresses, when plotted as in Figure 5, invariably fall precisely on the appropriate discontinuous arrays. Secondly, it is clear that swelling should favor the approach to equilibrium, but the discontinuities are no less marked for a rubber swollen with nearly 100 per cent of solvent than for the dry rubber.

ANISOTROPY IN THE ORIGINAL SHEET

It is conceivable that the departures from the theoretical form might arise from a difference of properties in different directions in the original sheet of rubber, introduced by the rolling process before vulcanization. Such an effect would arise from nonequilibrium or secondary linkages rother than from primary linkages, since the form of the stress-strain relations derived from the molecular theory is in no way dependent on the detailed structure of the molecular network[4]. If such anisotropy were present, it would be expected to reveal itself in a nonuniform swelling in different directions; but no such nonuniformity in swelling was observed. Furthermore, a latex rubber sheet, prepared by a quite different process not involving rolling or pressing, gave a precisely similar type of diagram to that of Figure 5. It is therefore concluded that an initial anisotropy cannot be responsible for the essential features of this diagram.

NONUNIFORMITY OF STRAIN

It has already been suggested that the guard-plate principle used in these experiments should eliminate any effect of nonuniformity of strain in the neighborhood of the edges of the sheet.

To check this point, experiments were made by two independent methods. The first was by the use of parallel strips in simple elongation, using values of force per unit area of the unstrained section equal to the values of f_1 and f_2 in the tables. The points derived from these experiments, separately marked in Figures 5 and 6, will be seen to fall exactly on the previously obtained arrays. The second check was obtained from measurements on a circular sheet clamped round its circumference and inflated. Details of the method have been described elsewhere[5]. This corresponds to the special case where $\lambda_1 = \lambda_2$. The experiment was made on the actual sheet of swollen rubber used to obtain the data of Figure 6. The results cannot conveniently be shown on this diagram, because the force could not simply be chosen to correspond to the values of f_1 and f_2 previously used. A plot of t_1 against $\lambda_1^2 - \lambda_3^2$, however, agreed to within 3 per cent with the data in Figure 6 for the case $f_1 = f_2$.

These independent experiments relating to the two extreme cases of simple elongation and 2-dimensional extension with $\lambda_1 = \lambda_2$ prove conclusively that the unexpected form of the results is not due to some defect in the technique of measurement. All the evidence suggests that the observed phenomenon represents a fundamental property of the rubber.

THEORETICAL INTERPRETATION OF DATA

Mooney[6] has discussed the form of the general stress-strain relations for a rubber on the basis of an assumed stress-strain relation in simple shear. For the particular case of a linear stress-strain relation in shear, he obtains, for the work of deformation:

$$W_2 = C_1(\lambda_1{}^2 + \lambda_2{}^2 + \lambda_3{}^2 - 3) + C_2 \left(\frac{1}{\lambda_1{}^2} + \frac{1}{\lambda_2{}^2} + \frac{1}{\lambda_3{}^2} - 3 \right) \qquad (3)$$

where C_1 and C_2 are physical constants of the material. The more general case of a nonlinear shear relation may be resolved by adding further terms to Equation (3). Thus the next term in the series would be of the type[7].

$$W_4 = A_4(\lambda_1{}^4 + \lambda_2{}^4 + \lambda_3{}^4 - 3) + B_r \left(\frac{1}{\lambda_1{}^4} + \frac{1}{\lambda_2{}^4} + \frac{1}{\lambda_3{}^4} - 3 \right) \qquad (4)$$

and the work of deformation would then be:

$$W = W_2 + W_4$$

From a rather more general standpoint, Rivlin[8] has argued that the work of deformation, or stored-energy function, must be a function of certain strain invariants, which are themselves symmetrical functions of the even powers of the extension ratios λ_1, λ_2 and λ_3. The simplest functions which may be chosen for the stored energy are:

$$W_1 = \tfrac{1}{2}G(\lambda_1{}^2 + \lambda_2{}^2 + \lambda_3{}^2 - 3) \qquad (5)$$

and

$$W_2 = \tfrac{1}{2}K \left(\frac{1}{\lambda_1{}^2} + \frac{1}{\lambda_2{}^2} + \frac{1}{\lambda_3{}^2} - 3 \right) \qquad (6)$$

Next in order of complexity are:

$$W_3 = L(\lambda_1{}^4 + \lambda_2{}^4 + \lambda_3{}^4 - 3) \qquad (7)$$

and

$$W_4 = M \left(\frac{1}{\lambda_1{}^4} + \frac{1}{\lambda_2{}^4} + \frac{1}{\lambda_3{}^4} - 3 \right) \qquad (8)$$

Rivlin's approach is perhaps simpler, and avoids the assumption that the form of the stress-strain relation for shear in an isotropic plane is independent of a stretch in the direction normal to that plane. However, the resultant stress-strain relations are the same whichever theory is adopted.

The stored-energy function derived from the molecular theory[1], from which Equations (2) and (2a) are obtained, is:

$$W = \tfrac{1}{2}G(\lambda_1{}^2 + \lambda_2{}^2 + \lambda_3{}^2 - 3) \qquad (9)$$

and is, therefore, equivalent to Mooney's equation (3) with the constant C_2 put equal to zero.

Let us now examine the stress-strain relations resulting from the first equation of Mooney (Equation (3)).   Corresponding to this stored-energy function, the principal stresses are given by Equation (25) in his paper, which may be written in the form[9]:

$$t_1 - t_3 = (G + L\lambda_2{}^2)(\lambda_1{}^2 - \lambda_3{}^2) \tag{10}$$

which, as will be seen, is a rather more complicated expression than Equation (2) derived from the molecular theory, using the stored-energy function (9).   In this expression, G and K are physical constants expressible in terms of C_1 and C_2 in Equation (3).   In the case when the forces per unit area of the unstrained rubber, F_1 and F_2 are given, and $F_3 = 0$, we have the following equations relating the strains with the forces (or stresses):

$$t_1 = \lambda_1 F_1 = (G + K\lambda_2{}^2)(\lambda_1{}^2 - \lambda_3{}^2)$$
$$t_2 = \lambda_2 F_2 = (G + K\lambda_1{}^2)(\lambda_2{}^2 - \lambda_3{}^2) \tag{10a}$$

These simultaneous equations enable the extension ratios to be determined when the applied forces F_1 and F_2 are given.   Their solution has been obtained graphically, using the particular values $G = 1.0$, $K = 0.1$, for six values of F_1 combined in all possible ways with the same values of F_2.   This solution is represented in Figure 7 in terms of the stress t_1 plotted against $\lambda_1{}^2 - \lambda_3{}^2$. Detailed comparison with Figure 6 shows a very close quantitative correspondence between the theoretical and experimental points.

Another method of comparing the experimental data with the theoretical Equation (10) is by plotting the experimental stress t_1 against $(1 + K\lambda_2{}^2/G)$ $\times (\lambda_1{}^2 - \lambda_3{}^2)$, choosing a suitable value of K/G.   This type of plot is shown in Figure 8, in which curve (b) relates to the swollen rubber.   With $K/G = 0.1$, the points fall very nearly on a straight line.

Thus Mooney's equation (3) gives a completely satisfactory representation of the behavior of this particular rubber in the swollen state.

It is interesting to examine some further properties of Mooney's equation. First, for a pure shear, we have one dimension (say λ_2) unchanged, and Equation (10) reduces to:

$$t_1 = (G + K)(\lambda_1{}^2 - \lambda_3{}^2)$$

In this case, therefore, the behavior is indistinguishable from that given by the simple equation $(2a)$.   Secondly, for the difference of the two principal stresses, in the general homogeneous strain, we have:

$$t_1 - t_2 = (G + K\lambda_3{}^2)(\lambda_1{}^2 - \lambda_2{}^2) \tag{10b}$$

If the forces are applied in the directions λ_1 and λ_2, the extension ratio corresponding to the thickness direction is always less than unity, and $\lambda_3{}^2$ is generally quite small.   If, therefore, K is also small compared with G, the term $K\lambda_3{}^2$ may be neglected, except at very small strains, i.e., Equation (10b) reduces to the simpler form (2).   This accounts for the observed linear relation between $t_1 - t_2$ and $\lambda_1{}^2 - \lambda_2{}^2$.

Turning now to dry rubber, we find rather a more complicated picture. By a suitable choice of K/G it is possible to represent the stress t_1 as a continuous function of $(1 + K\lambda_2{}^2/G)(\lambda_1{}^2 - \lambda_3{}^2)$, but this function is not linear (Figure 8(a)).   From this observation it is concluded that Mooney's equation represents a part, but not all of the deviation from the molecular theory (Equa-

tion 2a).   To account for the whole discrepancy it would probably be necessary to add further terms to the stored-energy function, such as those represented by Equations (7) or (8).   Since Mooney's equation (3) is based on a linear stress-strain relation in simple shear, it follows that the dry rubber is nonlinear in shear.   This fact may also be deduced by direct interpolation from the experimental data.   In other rubbers examined by the author, a nonlinear shear relation has been obtained[5], but Mooney[6] has reported a linear relation up to 200 per cent shear.

CONCLUSIONS

The conclusion to be drawn from the preceding analysis of the stress-strain relations may be summarized in the following way.   As a first approximation the equations derived from the statistical treatment of a molecular model provide a basis for the interpretation of the elastic properties of rubber.   A closer
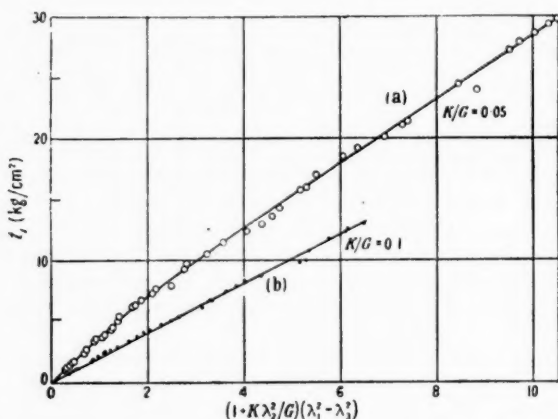
Fig. 8.—Data from Figures 5 and 6 plotted with $(1 + K\lambda_2{}^2/G)(\lambda_1{}^2 - \lambda_3{}^2)$ as abscissas. (a) Dry rubber, $K/G = 0.05$.   (b) Swollen rubber, $K/G = 0.1$.

approximation is obtained by including an additional term in the stored-energy function, i.e., by the use of Mooney's Equation (3).   This appears to give an accurate representation of the properties of a swollen rubber, but is still inadequate when applied to a dry rubber, for which a third approximation, including at least one more general term, is likely to be required.

It is necessary to emphasize that the use of the second or higher approximations does not in itself throw any light on the physical mechanism responsible for the behavior observed.   It is, in fact, the 3-dimensional analog of simple curve-fitting.   It must also be borne in mind that any physical model that might be postulated must necessarily lead to results which may be represented by some combination of the stored-energy functions discussed in the section on the theoretical interpretation of the data.

ACKNOWLEDGMENTS

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THE THERMODYNAMICS OF A STRAINED
ELASTOMER. I. GENERAL ANALYSIS *

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INTRODUCTION

This article is the first of a series, written by the present author and associates, devoted to the thermodynamics of strained elastomers. The first article is entirely theoretical and presents theory and equations to be applied in the analysis of experimental data.

A number of treatments of the thermodynamics of stretched rubber have been published. In most cases, the treatment presented was limited to that required for the analysis of a particular type of experimental data. The present treatment is intended to be general in scope and serve as the basis for analyzing any conceivable type of data having to do with the thermodynamic properties of a strained sample of a cured gum elastomer. It is assumed that the elastometer is isotropic in a sense later to be precisely defined, and that all deformations and changes of state are reversible.

Several points of view in the present analysis may be mentioned as being new. In the first place, recognizing that effects which occur with change in shape of an elastomer sample are usually of primary concern, whereas those occurring with change in volume are of secondary concern, we begin the analysis by assuming a volume equation of state which is sufficiently exact for our purpose. We assume that, at any deformation, the volume is a linear function of temperature and pressure. This neglect of second-order temperature and pressure effects seems to be entirely justified for the limited ranges of temperature and pressure involved in most experimental investigations. With this assumption regarding the volume, it then becomes possible to integrate the basic differential equations of thermodynamics and obtain explicit relationships between entropy, energy, and observed stresses or temperature changes in a deformed sample. If, at any time, experimental data become available which require inclusion of the second or higher terms of temperature and pressure, such terms can readily be included in a more exact analysis following the same procedure.

Another respect in which the present differs from previous treatments lies in the choice of the deformation variables. Following classical methods, the total strain is resolved into its two components, dilatation and pure shear, or change in volume and change in shape. Then, instead of length or dimension variables, we use deformation variables which refer exclusively to changes in shape and are independent of changes in volume.

Some elastomers crystallize when stretched. Certain limited thermodynamic analyses are valid in spite of any such change in phase composition which

may occur. In cases where this is not true, the analyses in the literature have been limited to low elongations or to types of elastomers which do not crystallize at any elongation. In the present analysis we take account of crystallization, subject to the assumption that percentage crystallinity, like the volume of the sample, is a linear function of pressure and temperature, and that the volume change resulting from crystallization is small.

The first of these assumptions would not be valid for raw Hevea and certain other elastomers which have, in the raw state, a fairly sharp melting point. Cured elastomers, on the other hand, have never been found to have a melting "point". Here again, the method of analysis can be carried through with higher powers of pressure and temperature retained if this is later found desirable. If a second-order transition occurs within the temperature range covered in a particular experiment, the slight changes in specific heat and coefficient of expansion would have, in many cases, only negligible effects. When, however, exact analysis is required, two solutions could be fitted to the experimental data, one on each side of the transition temperature.

Finally, as a further step beyond previous work, we incorporate in the present thermodynamic analysis the results obtained by the writer in a previous general treatment of the strain-work function for a large elastic deformation[1]. It is shown that this analysis of the work function can be applied generally to any thermodynamic function of a deformed elastomer, subject only to certain very mild conditions which are satisfied by nearly all cured elastomers.

Particular mention may be made at this point of the work of Elliott and Lippmann[2]. These authors were the first to recognize the theoretical importance of distinguishing between deformation at constant pressure and at constant volume. However, their treatment is limited to small deformations and is made somewhat awkward mathematically by the fact that they followed custom and used lengths to measure the deformation instead of the more suitable λ-variables employed in the present theory.

INDEX OF NOTATION

Subscripts; usual significance.

i, j, k—directions of principal strain and stress axes.
0—initial state of sample.
1, 2, 3—directions of principal strain and stress axes.
1—amorphous phase.
2—crystalline phase.

Variable	Eq. No.	Variable	Eq. No.	Variable	Eq. No.
f	9	A	4	α	20
h	58	C	36, 57, 58	β	15, 18–22
m	1	D	26	γ	60
r	5, 67	F	10, 79	δ	13
s	69	G	59	θ	33, 36, 58, 76
u	79	H	59	κ	15, 18–22
v	67, 71, 79	L	1	λ	6
w	79	P	9	μ	66
x	18, 30	Q	12	σ	9
		R	59	ϕ	35, 74
		S	28	ψ	33, 68
		T	15	ω	16, 19–22
		U	28	Φ	78
		V	1, 15, 17, 18	Ψ	78
		W	24, 52		
		X	44		
		Z	10		

ANALYSIS OF STRAIN

We consider an unstrained rectangular sample of a cured elastomer of mass m and dimensions L_{10}, L_{20}, L_{30}. If we represent by the V_0 the specific volume in the undeformed state at initial temperature and pressure, we may write:

$$mV_0 = L_{10}L_{20}L_{30} \qquad (1)$$

In the deformed state at any temperature and pressure, we have:

$$mV = L_1L_2L_3 \qquad (2)$$

We postulate, without loss in generality, that the three dimensions of the sample lie parallel to the principal strain axes. The principal strains are therefore $(L_i/L_{i0}) - 1$.

Obviously:

$$mdV = \sum_1^3 A_i dL_i$$

where

$$A_i = L_jL_k \qquad (4)$$

We now define r, the mean relative length, by the equation:

$$r = (V/V_0)^{\frac{1}{3}} \qquad (5)$$

and then introduce the deformation variables λ_i by the definition:

$$\lambda_i = (L_i/rL_{i0}) \qquad (6)$$

It follows directly from these defining equations that:

$$\lambda_1\lambda_2\lambda_3 = 1 \qquad (7)$$

$$\sum_1^3 (d\lambda_i/\lambda_i) = 0 \qquad (8)$$

The deformation variables λ_i, which we shall call the principal deformations, measure exclusively the change in shape of the sample, independent of changes in volume. Thus, Equation (6) states that λ_i is the ratio of the length in direction i to the length which the sample would have in the same direction if reduced to its original shape while retaining the same volume it has in the deformed state, at whatever temperature and pressure.

ANALYSIS OF STRESS

For later convenience, we shall employ separate notation for the atmospheric or hydrostatic pressure and the mechanical stresses used to deform the sample. In an isotropic material the stress axes coincide with the strain axes. We denote the principal mechanical stresses by f_i, the hydrostatic pressure by P, and the total stress by σ_i. Then:

$$\sigma_i = f_i - P \qquad (9)$$

In terms of F_i, the mechanical force, the mechanical stress, f_i, is:

$$f_i = F_i/A_i = \lambda_i Z_i/r^2 \qquad (10)$$

where Z_i is the conventional stress based on the original section, A_{i0}, or

$$Z_i = F_i/A_{i0} \tag{11}$$

The mean stress is:

$$Q = \tfrac{1}{3}\sum_1^3 \sigma_i = \tfrac{1}{3}\sum_1^3 f_i - P \tag{12}$$

and the effective deforming stresses are the stress deviations:

$$\delta_i = \sigma_i - Q \tag{13}$$

From these definitions it follows that

$$\sum_1^3 \delta_i = 0 \tag{14}$$

In the equations to be developed below, we shall use as our independent variables the deformation variables, λ_i, the mean stress, Q, and the absolute temperature, T.   The stress deviations, δ_i, are to be thought of as dependent variables, their values being determined by the mechanical reactions of the sample, while in the state of deformation λ_i at mean stress Q and temperature T.   There is a degree of the indeterminacy in the f_i, since each of them can be increased by an arbitrary amount, ϵ, without changing either Q or the δ_i, if at the same time P is also increased by ϵ.   This indeterminacy is generally resolved by some arbitrary condition in the experimental procedure, such as, for example, the use of a single deforming force applied in only one direction. With this procedure, P must then be considered as being adjusted in accordance with Equation (12) so as to give the independent variable Q arbitrarily assigned values.   Thus, if a deformation is to be carried out at constant Q, P must be varied so as to compensate continuously and exactly for variations in the mean mechanical stress, $\tfrac{1}{3}\sum f_i$.   Although actual experiments have not been and perhaps need never be carried out in this manner, it is nevertheless necessary to treat such a hypothetical experiment in the mathematical analysis.

VOLUME EQUATION OF STATE

In setting up an equation for the volume of the sample in terms of the independent variables, we wish to allow for the possibility of partial crystallization.   For each phase, amorphous and crystalline, we assume a volume equation which is linear in T and Q.   Thus, if we indicate the amorphous and crystalline phases by subscripts 1 and 2, respectively:

$$\left.\begin{aligned} V_1 &= V_{10}(1 + \beta_1\Delta T + \kappa_1\Delta Q) \\ V_2 &= V_{20}(1 + \beta_2\Delta T + \kappa_2\Delta Q) \end{aligned}\right\} \tag{15}$$

where V_{10} and V_{20} are the specific volumes at the reference temperature and mean stress, and β_1, β_2 and κ_1, κ_2 are, respectively, the thermal coefficients of expansion and the moduli of compressibility.   The constancy of β_1 and κ_1 at high deformations may be open to question.   We shall assume in the present analysis that any effects, so far unobserved, caused by variability of β_1 and κ_1, are negligible in comparison with the effects included in the analysis, all of which have been observed.

If we now represent by m_2 the mass in the crystalline state, the fractional mass is:

$$\omega = m_2/m \tag{16}$$

In accordance with assumptions previously stated, we write:

$$\omega = \omega_0 + \Delta\omega + (\partial\omega/\partial T)_{\lambda_i, Q}\Delta T + (\partial\omega/\partial Q)_{\lambda_i, T}\Delta Q \tag{17}$$

where:

$$\left.\begin{array}{l} \Delta\omega = \omega_{\lambda,0} - \omega_0 \\ \Delta T = T - T_0 \\ \Delta Q = Q - Q_0 \end{array}\right\} \tag{18}$$

Here the subscript 0 in ω_0 denotes the reference state, $\lambda_i = 1$, $T = T_0$, $Q = Q_0$; subscript $\lambda_i 0$ denotes a deformation λ_i at $T = T_0$, $Q = Q_0$. We note that the assumption of linearity in T and Q implies that the partial derivatives in Equation (7) must be constant within the experimental range involved.

The mean specific volume of the sample is:

$$V = V_1 + \omega(V_2 - V_1) \tag{19}$$

From Equations (15) to (19), it follows that, to the first approximation in the various volume increments:

$$V = V_0(1 + \alpha\Delta\omega + \beta\Delta T + \kappa\Delta Q) \tag{20}$$

in which:

$$V_0 = V_{10} + \omega_0(V_{20} - V_{10}) \tag{21}$$

$$\left.\begin{array}{l} \alpha V_0 = V_{20} - V_{10} \\ \beta V_0 = \beta_1 V_{10} + \omega_{x0}(\beta_2 V_{20} - \beta_1 V_{10}) + (V_{20} - V_{10})(\partial\omega/\partial T)_{\lambda_i, Q} \\ \kappa V_0 = \kappa_1 V_{10} + \omega_{x0}(\kappa_2 V_{20} - \kappa_1 V_{10}) + (V_{20} - V_{10})(\partial\omega/\partial Q)_{\lambda_i, T} \end{array}\right\} \tag{22}$$

It is to be noted that $\Delta\omega$, β, and κ are all functions of the deformation. $\Delta\omega$ is a function also of T and Q. Corresponding to Equation (20) we have, to the first approximation:

$$r = 1 + (\alpha\Delta\omega/3) + (\beta/3)\Delta T + (\kappa/3)\Delta Q \tag{23}$$

THE DIFFERENTIAL OF WORK

If we denote by dW the work done on unit mass in an infinitesimal change in strain, then:

$$mdW = \sum_1^3 (f_i - P)A_i dL_i \tag{24}$$

Now by applications of Equations (3) to (14), this expression for dW can be put into the forms:

$$dW = (1/m) \sum_1^3 (\delta_i + Q)A_i dL_i = QdV + V\sum_1^3 \delta_i(d\lambda_i/\lambda_i) \tag{25}$$

If we now let dD represent the increment in work associated with the stress deviations, we have:

$$dD = V\sum_1^3 \delta_i(d\lambda_i/\lambda_i) = V\sum_1^3 f_i(d\lambda_i/\lambda_i) = V_0\sum_1^3 rZ_i d\lambda_i \tag{26}$$

the latter forms of this equation being derived again by the application of Equations (8) to (14).

The expression for the total work increment now takes the form:

$$dW = QdV + dD \tag{27}$$

THE THERMODYNAMIC DIFFERENTIAL EQUATIONS

The first and second laws of thermodynamics are expressed by the equation:

$$TdS = dU - dW = dU - QdV - dD \tag{28}$$

where S and U are, respectively, the entropy and energy per unit mass. We wish to include in our treatment all possible types of deformation. In order to do this conveniently, we let x be a parameter which varies with extent of the deformation; and we suppose that each of the λ's is expressed as a function of x, the three functions being subject to the condition (7). Any possible path of deformation can thus be represented, while we have only a single deformation variable, x, to deal with directly in the following differential equations.

If we divide Equation (28) successively by the differentials ∂T, ∂Q, and ∂x, we obtain:

$$\left.\begin{array}{l} (\partial S/\partial T) = (1/T)[(\partial U/\partial T) - Q(\partial V/\partial T)] \\ (\partial S/\partial Q) = (1/T)[(\partial U/\partial Q) - Q(\partial V/\partial Q)] \\ (\partial S/\partial x) = (1/T)[(\partial U/\partial x) - Q(\partial V/\partial x) - (\partial D/\partial x)] \end{array}\right\} \tag{29}$$

In these and all subsequent equations it is to be understood, unless otherwise indicated, that a partial differentiation with respect to any of the variables T, Q, or x implies that the other two independent variables are constant in that differentiation. The derivatives $\partial D/\partial T$ and $\partial D/\partial Q$ are omitted in Equations (29) because, by Equation (26), the increment dD has no component in dT or dQ. It is obvious that:

$$\partial D/\partial x = \sum_1^3 (\partial D/\partial \lambda_i)(d\lambda_i/dx) = V_0 \sum_1^3 rZ_i(d\lambda_i/dx) \tag{30}$$

Now, by equating $\partial^2 S/\partial Q \partial T$ and $\partial^2 S/\partial T \partial Q$ derived from Equations (29.1) and (29.2), we obtain the equation:

$$(\partial U/\partial Q) = Q(\partial V/\partial Q) + T(\partial V/\partial T) \tag{31}$$

INTEGRATION OF THE EQUATIONS

The only dependent variable found in the right member of Equation (31) is V, for which we have assumed an equation of state. Hence, we substitute Equation (18) in (31) and obtain:

$$\partial U/\partial Q = V_0(\kappa Q + \beta T) \tag{32}$$

which can be integrated to yield:

$$U = V_0(\kappa/2)(Q^2 - Q_0^2) + V_0\beta T(Q - Q_0) + \theta(T - T_0) + \psi \tag{33}$$

θ and ψ are arbitrary functions of x. Since we are limiting ourselves to linear functions of T and Q, the arbitrary function of T takes the simple form indicated. Constants and arbitrary functions are chosen so that $U = 0$ in the reference state, $Q = Q_0$, $T = T_0$, $x = 0$. Obviously, ψ is the energy of deformation at Q_0, T_0.

Now substituting Equation (20) and (33) in Equations (29.1) and (29.2), we obtain a pair of partial differential equations:

$$\partial S/\partial T = (1/T)(\theta - \beta V_0 Q_0) \qquad \partial S/\partial Q = \beta V_0 \tag{34}$$

Integration leads to:

$$S = (\theta - \beta V_0 Q_0) \ln (T/T_0) + \beta V_0 (Q - Q_0)\, \mu\, \phi \tag{35}$$

in which ϕ is an arbitrary function of x. Again, the choice of arbitrary constants and the function ϕ is such that $S = 0$, in the reference state. Obviously, ϕ is the entropy of deformation at T_0, Q_0. Also, $\theta - \beta V_0 Q_0$ is the specific heat at constant x, and $Q = Q_0$, while θ is the specific heat at constant x and $Q = Q_0 = 0$. In later equations we shall set:

$$Q_{\lambda Q} = \theta - \beta V_0 Q_0 \tag{36}$$

Now to obtain D, we can first write (29.3) in the form:

$$\frac{\partial D}{\partial x} = \frac{\partial}{\partial x}(U - TS - QV) \tag{37}$$

We thus see that D is closely related to the Gibbs free energy, $U - TS + PV$; and in fact D is the free energy at constant mean stress, Q, in contrast to the free energy at constant atmospheric pressure, which is the Gibbs free energy.

If we were content to use D only in differential expressions such as Equation (37), it would be sufficient to set D equal to the parenthesis in this equation. However, following the logic of our method, we can make use of the arbitrary functions of integration to make D vanish at $x = 0$. Thus, we set:

$$D = U(x, T, Q) - TS(x, T, Q) - QV(x, T, Q)$$
$$\qquad - U(0, T, Q) + TS(0, T, Q) + QV(0, T, Q) \tag{38}$$

$$= \psi - T\phi - QV_0 \alpha \Delta\omega - V_0(\beta - \beta_0)\Delta T \Delta Q - \tfrac{1}{2}V_0(\kappa - \kappa_0)(\Delta Q)^2$$

where β_0 and κ_0 are the respective values in the undeformed state $x = 0$. Obviously, D is a linear function of T.

It is readily understood that D as defined by this equation is still the free energy at constant T and Q, except for an additive function of T and Q, which yields zero under the operation $(\partial/\partial x)_{T,Q}$. At the same time, D as defined here is the total work done by the deviatory stresses, δ_i, in producing deformation x at constant T and Q.

The last two terms of Equation (38) vanish if Q is Q_0, the reference mean stress. The term $QV_0 \alpha \Delta\omega$ represents the interchange of work between the deviatory stresses and the mean stress as a result of the change in volume $\alpha \Delta\omega$. This term vanishes at $Q = Q_0 = 0$, and in this case D reduces to $\psi - T\phi$.

The two functions ψ and ϕ are the functions of primary theoretical interest. We have seen here that they are directly related to the temperature-dependent and temperature-independent components of D, except for some small correction terms associated with certain changes in volume.

STRESS EQUATIONS

For the analysis of experimental data on deforming force as a function of temperature, stress equations are required which are derivable from the pre-

ceding equations.   In earlier work[1] it was shown that, in our present notation:

$$\sigma_i - \sigma_j = (1/V)[\lambda_i(\partial D/\partial \lambda_i) - \lambda_j(\lambda D/\partial \lambda_j)] \tag{39}$$

This equation was derived on the assumption of constant volume, but it is still valid in the present application with variable volume, since we have changed the definition of the λ_i so that Equations (7) and (8) still hold.   To express the stresses in terms more commonly used for elastomer systems, Equation (39) can be readily transformed into:

$$V_0 r(\lambda_i Z_i - \lambda_j Z_j) = \lambda_i(\partial D/\partial \lambda_i) - \lambda_j(\partial D/\partial \lambda_j) \tag{40}$$

This is a general equation, applicable to the deformation produced by any combination of stresses.   Let us consider the special case most commonly involved in experimental work, that in which the sample is stretched by a tensional force applied in only one direction, i.   Then $Z_j = Z_k = 0$, and:

$$\sigma_j = \sigma_k = -P, \qquad \lambda_j = \lambda_k = 1/(\lambda_i)^{\frac{1}{2}} \tag{41}$$

By means of Equation (41.2), D can be transformed into a function of λ_i only. Then, Equation (39) becomes:

$$\sigma + P = (\lambda/V)(\partial D/\partial \lambda) \tag{42}$$

the subscript i being omitted as being no longer necessary.   Likewise, Equation (40) becomes:

$$V_0 r Z = \partial D/\partial \lambda \tag{43}$$

If we now compare Equations (37) and (43), we see that rZ must be a linear function of T.   On the other hand, experimentalists report that Z is a linear function of T.   However, if rZ is strictly linear, the curvature in Z within the temperature range of reported experiments would not be detectable. Hence, the reported linearity of Z is no evidence against our deduction that rZ should be linear; and if we set:

$$X = rZ \tag{44}$$

we can expect experimental data to agree within experimental error with an equation of the form:

$$X = X_0(\lambda) + TX_1(\lambda) \tag{45}$$

From Equation (38) and later equations it follows that:

$$\left. \begin{array}{l} -(d\phi/d\lambda) = V_0(\partial X/\partial T) \\ d\psi/d\lambda = V_0[X - T(\partial X/\partial T) + V_0 Q\alpha(\partial \omega/\partial \lambda) \end{array} \right\} \tag{46}$$

and also:

$$V_0 X = (d\psi/d\lambda) - T(d\phi/d\lambda) - V_0 Q\alpha(\partial \omega/\partial \lambda) \tag{47}[3]$$

Equation (46) expresses the entropy and energy functions of primary interest in terms of the measurable quantities.   However, in applying these equations to stress measurements as usually made, certain corrections are required.   Evaluation of the derivative $\partial X/\partial T$ requires the temperature variation of X at constant λ and Q; whereas measurements are actually made with unidirectional stretching force at constant P instead of constant Q; and usually at constant L instead of constant λ.

We seek a correction formula for converting a measurement at $T = T_0 + \Delta T$, $\lambda = \lambda_a + \Delta\lambda$, $Q = Q_a + \Delta Q$ to the measurement which would be obtained at $T = T_0 + \Delta T$, $\lambda = \lambda_a$, $Q = Q_a$. The subscript a signifies a reference state other than $Q = Q_0$, $\lambda = 0$. $\Delta\lambda$ and ΔQ are here the increments caused by the imposed change ΔT under the customary experimental conditions of constant P and L. We begin with the general equation:

$$X(\lambda, T, Q) = X(\lambda_a, T, Q_a) + (\partial X/\partial\lambda)_{T,Q}\Delta\lambda + (\partial X/\partial Q)_{\lambda,T}\Delta Q \quad (48)$$

We have, making use of Equations (80.4) and (81.2) in Appendix II:

$$\left| \Delta\lambda = \frac{L_a}{L_0}\frac{\partial}{\partial T}\left(\frac{1}{r}\right)_{L,P}\Delta T \doteq -\lambda_a\left[\frac{\beta}{3} + \frac{\kappa\lambda}{9}\left(\frac{\partial X}{\partial T}\right)_{\lambda,P}\right]\Delta T \quad (49)\right.$$

$$\left| \Delta Q = \left(\frac{\partial Q}{\partial T}\right)_{L,P}\Delta T \doteq \frac{\lambda_a}{3}\left(\frac{\partial X}{\partial T}\right)_{\lambda,P}\Delta T\right.$$

To a sufficient approximation in the correction terms:

$$(\partial X/\partial\lambda)_{T,Q} \doteq (\partial X/\partial\lambda)_{T,P}$$
$$(\partial X/\partial Q)_{\lambda,T} = -\alpha(\partial\omega/\partial\lambda) \quad (50)$$

From (48), (49), and (50):

$$X(\lambda_a, T, Q_a) = X(\lambda, T, Q)$$
$$+ \Delta T\left\{\left(\frac{\partial X}{\partial\lambda}\right)_{T,P}\left[\frac{\beta\lambda_a}{3} + \frac{\kappa\lambda_a^2}{9}\left(\frac{\partial X}{\partial T}\right)_{\lambda,P}\right] + \frac{\alpha\lambda_a}{3}\frac{\partial\omega}{\partial\lambda}\left(\frac{\partial X}{\partial T}\right)_{\lambda,P}\right\} \quad (51)$$

In experiments of the kind under discussion, the correction terms in α and κ are small compared to the term in β. As an adequate correction formula we therefore have:

$$X_a = X(\lambda_a, T, Q_a) = X(\lambda, T, Q) + (\beta\lambda_a/3)(\partial X/\partial\lambda)_{T,P}\Delta T \quad (52)$$

X_a, substituted for rZ in Equation (46), now gives correct expressions for $d\phi/d\lambda$ and $d\psi/d\lambda$ in terms of observables. But a word of caution is necessary regarding the derivative $(\partial X/\partial\lambda)_{T,P}$. The $\Delta\lambda$ involved in this case is always quite small, and Wiegand and Snyder[4] have shown that the slope in a small stress-strain cycle is appreciably greater than the local slope of the total stress-strain curve. The same statement would apply to X or rZ, which signifies that $\partial X/\partial\lambda$ for the correction formula (51) should be determined by measurements in a short cycle of deformation.

TEMPERATURE EQUATION

The equation for the Joule heat effect, or temperature change in adiabatic reversible strain, involves a number of small correction terms. The type of strain normally employed in such experiments is that produced by a unidirectional tension imposed in an atmosphere of constant pressure. We limit the following analysis to this case, and we write, for an adiabatic deformation:

$$(\partial S/\partial\lambda)_P \equiv (\partial S/\partial\lambda)_{T,Q} + (\partial S/\partial Q)_{\lambda,T}(\partial Q/\partial\lambda)_{S,P}$$
$$+ (\partial S/\partial T)_{\lambda,Q}(\partial T/\partial\lambda)_{S,P} = 0 \quad (53)$$

In this equation, $(\partial T/\partial\lambda)_{S,P}$ is the measured effect. Approximate expressions for the other partial derivatives are given in Appendix II. Substituted into

Equation (53) they lead to the result:

$$-\frac{d\phi}{d\lambda} = V_0 \left(\frac{\partial X}{\partial T}\right)_{\lambda,Q}$$

$$= \left(\frac{\partial T}{\partial \lambda}\right)_{S,P} \left[\frac{C_{\lambda Q}}{T} + \frac{\beta\lambda V_0}{3}\left(\frac{\partial Z}{\partial T}\right)_{\lambda,P}\right] + \frac{\beta V_0}{3}\left[Z + \lambda\left(\frac{\partial Z}{\partial \lambda}\right)_{T,P}\right]$$

$$= \left(\frac{\partial T}{\partial \lambda}\right)_{S,P} \left[\frac{C_{LP}}{T} - \frac{\beta\lambda V_0}{3}\left(\frac{\partial Z}{\partial T}\right)_{\lambda,P} - \frac{\kappa\lambda^2 V_0}{9}\left(\frac{\partial Z}{\partial T}\right)_2^{\lambda,P}\right]$$

$$+ \frac{\beta V_0}{3}\left[Z + \lambda\left(\frac{\partial Z}{\partial \lambda}\right)_{T,P}\right] \quad (54)$$

$$C_{LP} = C_{\lambda Q} + T[(2\beta V_0\lambda/3)(\partial Z/\partial T) + (\kappa\lambda^2 V_0/9)(\partial Z/\partial T)^2] \quad (55)$$

The specific heat at constant $Q = Q_0$, represented by θ, arose as an arbitrary function of x in Equation (37). It is obvious, however, that θ can be expressed in terms of the specific heats of the amorphous and crystalline phases, C_{10} and C_{20}, the latent heat of crystallization, h, the phase composition, ω, and rate of change of ω with T. Thus:

$$\theta = C_{10} + \omega(C_{20} - C_{10}) - h(\partial\omega/\partial T)_{\lambda,Q} \quad (56)$$

It is not necessary to assume here that h is independent of λ and Q.

THE GENERAL FORM OF DEFORMATION FUNCTIONS

The general form of the strain-work function was derived on the assumption of constant volume[2]. The same derivation applies also to the case of variable volume if we let the λ_i be the principal deformations, instead of the principal strains, with the result that Equation (7) still holds. Consequently, we conclude that ϕ and ψ, which express the variation of D with the deformations λ_i, must each have the general form given by Equation (47) of the earlier work[1]. This form is:

$$R(\lambda_i) = \sum_{n=1}^{\infty}\left[\frac{G_{2n}}{4n}\sum_{i=1}^{3}(\lambda_1^{2n} + 1/\lambda_i^{2n} - 2) + \frac{H_{2n}}{4n}\sum_{i=1}^{3}(\lambda_i^{2n} - 1/\lambda_i^{2n})\right] \quad (57)$$

in which G_{2n} and H_{2n} are constants. G_2 is the temperature-dependent or the temperature-independent component of the modulus of rigidity for moderate deformations, depending on whether R represents ψ or ϕ. In general, R contains, in addition to the terms in Equation (57), a constant term $R_0 \neq 0$. Also, in general, the parameters G_{2n} and H_{2n} are functions of T and Q.

If the deformation is a simple shear of magnitude, γ, R can be expressed in the form, Equation (49)[1]:

$$R(\gamma) = \sum_{q=1}^{\infty}\frac{\gamma^{2q}}{(2q)!}\sum_{n=q}^{\infty}\frac{G_{2n}}{n}n^2[n^2 - 1^2]\cdots[n^2 - (q-1)^2] \quad (58)$$

The proof that ϕ and ψ, the entropy and energy of deformation, must have the form of (57), is indirect; for the initial assumptions in the proof were related to stress-strain relationships, the connection with entropy and energy being established through necessary relationships between stresses, work of deformation, and entropy and energy of deformation. This question naturally arises: What assumptions or postulates must be made regarding ϕ, ψ, themselves, or

any other function of deformation, in order to arrive at the functional forms (57) and (58)?

It is sufficient to make the following postulates concerning the elastomer material and the deformation function considered. Such an elastomer and such a deformation function may, for convenience, be referred to as "normal".

1. The elastomer is isotropic in the unstrained state and, in any state of strain having axial symmetry, remains isotropic in the plane normal to the symmetry axis.

2. In any strain the deformation function considered is an analytic function of the deformation variables, λ_i, over the range of physically attainable λ_i. In any simple shear in an isotropic plane, this function is expressible as an even power series in the shear, γ.

3. The specific volume of the material conforms to postulates 1 and 2.

The proof that these three postulates lead to the deformation functions (57) and (58) is given in Appendix I.

The symmetry required by the postulate 1 means that the power series in γ referred to in postulate 2 must be either even or odd and cannot be mixed. Since for every even function, $R(\gamma)$, there is also an odd function, $dR/d\gamma$, and *vice versa*, our choice of an even power series in postulate 2 does not reduce the number of functions of deformation covered by our analysis. This choice of an even function corresponds, for example, to a choice of the work, instead of the deforming stress, as the deformation function to which the postulates apply. The analysis in any case applies directly to an even function of γ.

If a deformation is produced by a unidirectional tension or pressure, so that the deformation is characterized by Equation (41), then Equation (57) reduces to:

$$R(\lambda) = \sum_{n=1}^{\infty} \frac{G_{2n}}{4n} \left[\lambda^{2n} + \frac{1}{\lambda^{2n}} + 2 \left(\lambda^n + \frac{1}{\lambda^n} \right) - 6 \right] + \sum_{n=1}^{\infty} \frac{H_{2n}}{4n} \left[\lambda^{2n} - \frac{1}{\lambda^{2n}} - 2 \left(\lambda^n - \frac{1}{\lambda^n} \right) \right] \quad (59)$$

If the deformation function is adequately represented, within a limited range of deformation, by the first terms only; *i.e.*, for $n = 1$, Equations (57) to (59) then reduce to:

$$R(\lambda_i) = \frac{G}{4} \sum_{i=1}^{2} \left(\lambda_i^2 + \frac{1}{\lambda_i^2} - 2 \right) + \frac{H}{4} \sum_{i=1}^{3} \left(\lambda_i^2 - \frac{1}{\lambda_i^2} \right) \quad (60)$$

$$R(\gamma) = (G/2)\gamma^2 \quad (61)$$

$$R(\lambda) = \frac{G}{4} \left[\lambda^2 + \frac{1}{\lambda^2} + 2 \left(\lambda + \frac{1}{\lambda} \right) - 6 \right] + \frac{H}{4} \left[\lambda^2 - \frac{1}{\lambda^2} - 2 \left(\lambda - \frac{1}{\lambda} \right) \right] \quad (62)$$

It seems appropriate at this point to state, without proof, certain facts concerning the applicability of the operator Equations (39) or (40), and (42) or (43). It is obvious that the inherent symmetry of Equation (59) in the λ_i is formally destroyed if any one of the three λ_i's is eliminated by a substitution $\lambda_i = 1/\lambda_j \lambda_k$. It is interesting to find that if now the operations indicated in Equations (39) or (40) are applied to the transformed deformation function, the result is still correct. This means, for example, that $\sigma_i - \sigma_j$ as expressed

by Equation (39) is invariant under any transformation of D permitted by Equation (7).

With regard to the operator Equations (42) and (43), the situation is somewhat different. If the deformation considered is subject to any condition, $F(\lambda_1, \lambda_2, \lambda_3) = 0$, in addition to Equation (7), then the deformation function can be reduced to a function of only one of the λ_i, such as Equation (59) or (62). However, the only case in which the single-term operator of Equation (42) is valid is the particular case represented by condition (41).

Here the condition $\sigma_j = \sigma_k$ is necessary, but not $\sigma_j = 0$. If $\sigma_j = \sigma_k \neq 0$, Equation (42) has the slightly more general form:

$$\sigma_i - \sigma_j = (\lambda_i/V)[dD(\lambda_i)/d\lambda_i] \tag{63}$$

DISCUSSION

Previous thermodynamic analyses of strained elastomers have been developed in terms of the strain variables, L_i/L_{i0} (principal strain $+1$). Our choice of the deformation variables L_i/rL_{i0}, has led naturally and easily to two important consequences; first, that the entropy and energy of strain are separated, respectively, into entropy and energy of deformation, and other terms representing effects of pressure, temperature and dilatation; second, that the entropy and energy of deformation must each have the form of a particular multiparameter function of the principal deformations, provided only that the undeformed elastomer is isotropic and normal, as defined in this paper.

These consequences, aside from their scientific interest, have a certain practical value in the analysis of data. With foreknowledge of the necessary form of the entropy and energy functions of deformation, the task of fitting curves to experimental data is reduced to the determination of certain parameters to give the best fit.

The conclusion that such a variable as ω, the fractional crystallinity, can be represented by the general deformation function does not imply that the curve of ω versus deformation should resemble the curve for the work of deformation. The form of a particular deformation function varies greatly with the values assigned to the parameters in the function. Also, the form may vary with temperature and mean stress, since the parameters may be functions of T and Q.

The properties of an elastomer which have been defined as normal are to be expected unless there is some peculiarity in the curing procedure which causes anisotropy in the cured material. On the other hand, reversibility in stress-strain cycles, assumed in the analysis, does not exist in reality. The experimentalist must use special techniques to attain even approximate reversibility; and it is still an open question whether the techniques employed have been as adequate as they seemed. This point will be discussed further in later communications.

A number of synthetic elastomers are known which, when stretched, give x-ray diffraction patterns indicating ordered states of incomplete regularity, as compared with the crystalline state, having 3-dimensional periodicity. To apply the present analysis to such elastomers, it is necessary only to assume a density change and latent heat in the transition from the amorphous to the semi-ordered state.

Equations (46) show that the entropy and energy of deformation are more directly related to X, or rZ, then to Z itself. This is understandable if we recognize that, to produce a given change in deformation, a given force, A_0Z

must act through a distance which is proportional to r, $r - 1$ being the mean linear expansion of the sample.

In articles which are to follow the present theoretical analysis, the equations developed are applied to experimental data and conclusions are drawn regarding the thermodynamic properties of various cured elastomers.

APPENDIX I

PROOF OF GENERAL VALIDITY OF THE DEFORMATION FUNCTION

We assume the validity of the preceding postulates 1–3. The principal stretch variables, μ_i, are defined by:

$$\mu_i = L_i/L_0 = r\lambda_i \tag{64}$$

We shall consider a general state of strain as being produced in two steps, a and b. In the first step the strain is such as is produced by a unidirectional stress in direction 1. Then we have the relations:

$$\mu_1\mu_n{}^2 = v_a = r_a{}^3 \qquad \mu_1 = r_a\lambda_a \tag{65}$$

where μ_n is the stretch in the 2–3 plane, and v_a is the relative volume in state a.

By postulate 2, any deformation function, R, will vary continuously with the strain, and for the step a we may write:

$$\Delta R_a = \psi(\lambda_a) \tag{66}$$

ψ being an unknown analytic function of λ_a.

Now to complete the general deformation, we impose a shear, γ, in the 2,3 plane while holding L_1 constant. The shear is related to s_2 and s_3, the principal deformations in the 2–3 plane referred to state a, by the equation:

$$\gamma = s_2 - s_3 \tag{67}$$

By definition of a principal deformation, we must have:

$$s_2 s_3 = 1 \tag{68}$$

If we denote by μ_2, μ_3 the final 2, 3 stretches, and by v_b the volume expansion in step a to b, we must have:

$$\mu_2 = s_2 v_b{}^{\frac{1}{2}}\mu_n \qquad \mu_3 = s_3 v_b{}^{\frac{1}{2}}\mu_n \tag{69}$$

Hence

$$\mu_2\mu_3 = v_b\mu_n{}^2 = v_a v_b/\mu_1$$
$$\mu_1\mu_2\mu_3 = v_a v_b = r_a{}^3 r_b{}^3 = r^3 \tag{70}$$
$$\mu_i = r\lambda_i$$

r being the mean linear expansion in state b compared with the undeformed state.

Now by appropriate substitution in Equation (69), we find:

$$\gamma^2 = \lambda_1(\lambda_2 - \lambda_3)^2 \tag{71}$$

The change produced in R by the change in strain from state a to state b is, by postulate 2, expressible as a power series in γ^2. The coefficients in this series will depend upon the extent of the deformation in state a. The total change in R will therefore be of the form:

$$\Delta R = \psi(\lambda_a) + \sum_1^\infty \phi_n(\lambda_a)\lambda_1{}^n(\lambda_2 - \lambda_3)^{2n} \tag{72}$$

We must now eliminate λ_a from this equation. From preceding equations:

$$\lambda_1 = \frac{\mu_1}{r} = \frac{r_a \lambda_b}{r_a r_b} = \frac{\lambda_a}{r_b} \tag{73}$$

By postulate 3:

$$r_b = 1 + \sum_1^\infty \theta_n(\lambda_a)\gamma^{2n} \tag{74}$$

where the coefficients θ_n are such that this series is convergent and analytic. We can now express λ_a in the form:

$$\lambda_a = \lambda_1\left[1 + \sum_1^\infty \theta_n\gamma^{2n}\right] \tag{75}$$

Substitution into (72) gives an expression for ΔR which can be written in the form:

$$\Delta R = \Psi(\lambda_1) + \sum_1^\infty \Phi(\lambda_1)(\lambda_2 - \lambda_3)^{2n} \tag{76}$$

We have thus reduced ΔR to the same form as Equation (34) of reference 1. This condition, together with equation $\lambda_1\lambda_2\lambda_3 = 1$, is all that is mathematically required in the derivation of the general deformation function $R(\lambda_i)$.

SUMMARY

The thermodynamic functions of principal interest in a strained elastomer are the entropy and energy of deformation. The volume is of secondary importance, and it can be assumed, with sufficient accuracy for most purposes, that the volume is linear in the temperature and the mean pressure. The basic partial differential equations of thermodynamics can then be integrated, yielding expressions for the energy and entropy of deformation in terms of observable quantities.

In the present analysis the volume effects caused by changes in mean pressure and crystallinity are taken into account, and the effects associated with change in shape are sharply separated from those associated with change in volume. It is shown that the superelastic functions of deformation previously published[1] have a very general validity.

APPENDIX II

APPROXIMATE EQUATIONS FOR PARTIAL DERIVATIVES

The following expressions for certain selected partial derivatives apply to the strains produced by a unidirectional stretching force. They are obtained in most cases by means of general formulas of the type:

$$(\partial F/\partial u)_c = (\partial F/\partial u)_{v,w} + (\partial F/\partial v)_{w,u}(dv/du)_c + (\partial F/\partial w)_{u,v}(dw/du)_c \tag{77}$$

where u, v, w represent T, Q, and X or λ_i and the subscript c signifies any experimental condition which fixes the variation of v and w with u. The approximations are carried, as a rule, to the first degree in α, β, and κ and the partial derivatives $(\partial\omega/\partial T)_{\lambda,Q}$ and $(\partial\omega/\partial Q)_{\lambda,T}$. Even the first-degree terms are omitted in the expressions for the derivatives of Q, Equations (79), since

these expressions, in application, are combined with κ. It is frequently helpful to remember that, to the first approximation, it makes no difference in the following derivatives whether c signifies constant L or constant λ. Also, since approximately $X = Z$, X and Z may be interchanged at will in any term having α, β, or k as a factor.

$$r = 1 + \tfrac{1}{3}(\alpha\Delta\omega + \beta\Delta T + \kappa\Delta Q) \tag{23}$$

$$= 1 + \tfrac{1}{3}[\alpha\Delta\omega + \beta\Delta T + (k\lambda Z/3)] \tag{53}$$

$$\left.\begin{aligned}
(\partial r/\partial\lambda)_{T,Q} &= (\alpha/3)(\partial\omega/\partial\lambda)_{T,Q} \\
(\partial r/\partial\lambda)_{T,P} &= (\alpha/3)(\partial\omega/\partial\lambda)_{T,Q} + (\kappa/9)[Z + \lambda(\partial Z/\partial\lambda)_{T,P}] \\
(\partial r/\partial T)_{\lambda,Q} &= \beta/3 \\
(\partial r/\partial T)_{\lambda,P} &= (\beta/3) + (\kappa\lambda/9)(\partial Z/\partial T)_{\lambda,P} \\
(\partial r/\partial Q)_{\lambda,T} &= \kappa/3
\end{aligned}\right\} \tag{78}$$

$$Q = (\lambda Z/3r^2) - P \tag{12}$$

$$\left.\begin{aligned}
(\partial Q/\partial\lambda)_{T,P} &= \tfrac{1}{3}[Z + \lambda(\partial Z/\partial\lambda)_{T,P}] + \cdots \\
(\partial Q/\partial T)_{L,P} &= (\lambda/3)(\partial Z/\partial T)_{\lambda,P} + \cdots \\
(\partial Q/\partial\lambda)_{S,P} &= \tfrac{1}{3}[Z + \lambda(\partial Z/\partial\lambda)_{T,P}] + (\lambda/3)(\partial Z/\partial T)_{\lambda,P}(\partial T/\partial\lambda)_{S,P} + \cdots
\end{aligned}\right\} \tag{79}$$

$$\lambda = L/rL_0 = (L/L_0)[1 - \tfrac{1}{3}(\alpha\Delta\omega + \beta\Delta T + \kappa\Delta Q)]$$
$$= L/L_0[1 - \tfrac{1}{3}(\alpha\Delta\omega + \beta\Delta T + (\kappa\lambda Z/3))] \quad \text{(for } \Delta P = 0) \tag{6}$$

$$\left.\begin{aligned}
(\partial\lambda/\partial T)_{L,Q} &= -\beta\lambda/3, \\
(\partial\lambda/\partial T)_{L,P} &= -(\beta\lambda/3) - (\kappa\lambda^2/9)(\partial Z/\partial T)_{\lambda,P}
\end{aligned}\right\} \tag{80}$$

$$X = rZ \tag{44}$$

$$\left.\begin{aligned}
(\partial X/\partial Q)_{\lambda,T} &= -\alpha(\partial\omega/\partial\lambda)_{T,Q}, \quad \text{(by Eq. (47))} \\
(\partial X/\partial\lambda)_{T,Q} &= r(\partial Z/\partial\lambda)_{T,Q} + (\alpha Z/3)(\partial\omega/\partial\lambda)_{T,Q} \\
(\partial X/\partial\lambda)_{T,P} &= r(\partial Z/\partial\lambda)_{T,P} + (\kappa/9)[Z^2 + \lambda Z(\partial Z/\partial\lambda)_{T,P}] \\
&\qquad\qquad + (\alpha Z/3)(\partial\omega/\partial\lambda)_{T,P} \\
&= r(\partial Z/\partial\lambda)_{T,Q} - (\alpha\lambda/3)(\partial\omega/\partial\lambda)_{T,Q}(\partial Z/\partial\lambda)_{T,P} \\
&\qquad\qquad\qquad\qquad\qquad\qquad \text{(by Eq. (81.1))} \\
(\partial X/\partial T)_{\lambda,Q} &= r(\partial Z/\partial T)_{\lambda,Q} + \beta Z/3 \\
(\partial X/\partial T)_{\lambda,P} &= r(\partial Z/\partial T)_{\lambda,P} + (\beta Z/3) + (\kappa\lambda Z/9)(\partial Z/\partial T)_{\lambda,P} \\
&= r(\partial Z/\partial T)_{\lambda,Q} + \beta Z/3 - (\alpha\lambda/3)(\partial\omega/\partial\lambda)_{T,Q}(\partial Z/\partial T)_{\lambda,Q} \\
(\partial Z/\partial Q)_{\lambda,T} &= -\kappa Z/3 - \alpha(\partial\omega/\partial\lambda)_{T,Q}{}^* \\
(\partial Z/\partial\lambda)_{T,P} &= (\partial Z/\partial\lambda)_{T,Q} - [(\kappa Z/3) - \alpha(\partial\omega/\partial\lambda)_{T,Q}][Z + \lambda(\partial Z/\partial\lambda)_{T,Q}]
\end{aligned}\right\} \tag{81}$$

$$\left.\begin{aligned}
(\partial Z/\partial T)_{L,P} &= (\partial Z/\partial T)_{\lambda,Q}[1 - (\kappa\lambda Z/9) - (\alpha\lambda/3)(\partial\omega/\partial\lambda)_{T,Q}] \\
&\quad - (\partial Z/\partial\lambda)_{T,P}[(\beta\lambda/3) + (\kappa\lambda^2/9)(\partial Z/\partial T)_{\lambda,P}] \\
(\partial Z/\partial T)_{\lambda,P} &= (\partial Z/\partial T)_{\lambda,Q}[1 - (\kappa\lambda Z/9) - (\alpha\lambda/3)(\partial\omega/\partial\lambda)_{T,Q}
\end{aligned}\right\} \tag{82}$$

$$S = C_{\lambda Q}\ln(T/T_0) + \beta V_0(Q - Q_0) - \phi \tag{35}$$

$$C_{\lambda Q} = \theta - \beta V_0 Q_0 \tag{36}$$

$$\left.\begin{aligned}
(\partial S/\partial\lambda)_{T,Q} &= d\phi/\partial\lambda = -V_0(\partial X/\partial T)_{\lambda,Q} \\
(\partial S/\partial Q)_{T,\lambda} &= \beta V_0 \\
(\partial S/\partial T)_{\lambda,Q} &= \theta - \beta V_0 Q_0/T = C_{\lambda Q}/T
\end{aligned}\right\} \tag{83}$$

* Obtained by substituting $X = rZ$ in (83.1).

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THE THERMODYNAMICS OF A STRAINED
ELASTOMER. II. COMPRESSIBILITY *

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INTRODUCTION

In the first paper of this series[1], a number of equations were developed which included the coefficients of compressibility and thermal expansion as parameters. To apply such equations in the analysis of experimental data on thermoelasticity, it is obviously necessary to know the values of these parameters for the different polymers and for different states of deformation. The present paper deals primarily with the compressibilities of a group of polymers at zero deformation. Certain incidental associated data also are presented, including the effect of elongation up to 200 per cent of the thermal expansion of a Hevea gum stock.

APPARATUS AND METHOD

The apparatus for measuring the compressibility consists of a water-jacketed chamber, A, $\frac{9}{16}$ inch inside diameter, 15 inches long, and made of Shelby steel tubing. The bottom of the chamber is connected through a valve, B, to a high pressure oil pump, C, while the top of the chamber is connected through a second valve, D, to a burette, E. A pressure gauge, F, is placed in the line connecting the chamber to the pump (Figure 1).

The elastomer sample, S, used for the determination of compressibility was cured in the form of a round rod $\frac{1}{2}$ inch in diameter and about 14 inches long. It was placed in the chamber and oil pumped through the chamber and overflow pipe, G, until the air was swept out of the system so far as possible. The oil was a standard hydraulic fluid which had no measureable effect on the rubber during the time of the experiment. Removal of air was facilitated by wetting the sample with oil before placing it in the apparatus. It was also found that closing the upper valve, D, pumping oil into the system until the pressure was between 5000 and 10,000 lb. per sq. in., and then suddenly releasing the pressure by opening the upper valve, aided in removing the air. When it was evident that no more air could be removed, the oil level was adjusted to the zero mark on the burette with the upper valves, D and G, closed. The pressure was then raised to a predetermined value, the lower valve closed and the upper valve, D, opened. In this manner pressure was applied to the sample and released in a comparatively short time, less than 20 seconds. The increase in volume of the oil and rubber in returning to atmospheric pressure was read in the burette after closing the valve, D. The measurement was repeated three times at each pressure. The pressure was increased in steps of 500 lb. per sq. in. up to 5000 lb. per sq. in.
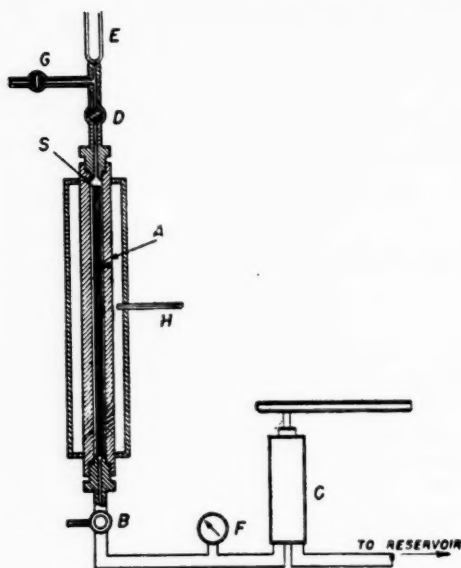
Fig. 1.

A thermometer, H, was kept in the water jacket, but no change in temperature was observed during the course of any experiment. Since the change in pressure from atmospheric to P and back to atmospheric was so rapid, the compressibility observed was the adiabatic compressibility.

It is obvious that the observed increase in volume is due in part to the compressibility of (1) the oil, (2) any air bubbles present in the system, and (3) the rubber. Consecutive tests on the same sample showed that the swelling by the oil was too small to influence the results. The compressibility of the oil may be obtained by comparing the volume changes obtained with oil alone in the chamber to those obtained with a steel rod as the sample. The compressibility of the steel is so small it may be considered zero.

METHOD OF ANALYSIS

The apparatus was not designed to obtain a high degree of accuracy, but when the data for rubber were plotted, the curvature appeared to be significant. Consequently, a method of analysis of the data was used which would take advantage of the unexpected precision.

Assume a volume of residual air in the system equal to A_0 in the case of oil, A_s when the steel rod is in the system, and A_r with the rubber sample. We assume that the air behaves as a perfect gas compressed isothermally; and we express the pressure in lb. per sq. in. Then, with oil in the chamber at pressure P:

$$A_0 \frac{14.7}{P + 14.7} + \left(V_c - A_0 \frac{14.7}{P + 14.7} \right) = V_c \tag{1}$$

After releasing the pressure P:

$$A_0 + \left(V_c - A_0 \frac{14.7}{P + 14.7} \right) (1 + A_0 P + b_0 P^2) = V_c + M_0 \tag{2}$$

where c' = volume of chamber (cc.), P = pressure, lb./in.^{2} above atmospheric, M_0 = observed increase in volume of oil in the burette, and a_0 and b_0 = compressibility coefficients of the oil defined by:

$$V = V_0[(1 - a_0P - b_0P^2)] \tag{3}$$

These two equations give:

$$A_0 \frac{P}{14.7 + P} + \left(V_c - A_0 \frac{14.7}{P + 14.7} \right)(a_0P + b_0P^2) = M_s \tag{4}$$

Similarly, with the steel rod:

$$A_s \frac{P}{P + 14.7} + \left(V_c - V_s - A_s \frac{14.7}{P + 14.7} \right)(a_0P + b_sP^2) = M_s \tag{5}$$

where V_s = volume of steel rod, and M_s = observed volume increase with steel rod in the chamber. Solution of these last two equations gives:

$$(A_0 - A_s) + [V_s(P + 14.7) - (A_0 - A_s)14.7]$$
$$\times [a_0 + b_0P] = (M_0 - M_s)\left(\frac{P + 14.7}{P} \right) \tag{6}$$

or

$$y = a + bP + cP^2 \tag{7}$$

where

$$\begin{aligned}
y &= M_0 - M_s[P + 14.7/P] \\
a &= (A_0 - A_s)(1 - 14.7a_0) + 14.7V_sa_0 \\
b &= V_sa_0 + 14.7b_0[V_s - (A_0 - A_s)] \\
c &= V_sb_0
\end{aligned} \tag{8}$$

from which:

$$\begin{aligned}
b_0 &= c/V_s \\
a_s &= b/V_s
\end{aligned} \tag{9}$$

since the second term in the equation for b may be neglected.

As P was varied in equal steps, the second-degree equation in P was easily fitted to the data by using orthogonal polynomials[2].

The same method of analysis for the system containing rubber leads to:

$$A_r \frac{P}{14.7 + P} + \left(V_c - V_r[1 - a_rP - b_rP^2] - A_r \frac{14.7}{P + 14.7} \right)$$
$$\times (a_0P + b_0P^2) = M_r \tag{10}$$

Solution of (6) and (10) gives an equation of the form:

$$y = k + BP + CP^2 + DP^3 + EP^4 \tag{11}$$

where:

$$\begin{aligned}
y &= (M_r - M_s)[(P + 14.7)/P] \\
k &= 14.7V_ra_r + (A_r - A_s)(1 - 14.7a_0) + 14.7a_0(V_s - V_r) \approx A_r - A_s \\
B &= V_ra_r(1 + 14.7a_0) + 14.7V_rb_r + a_0(V_s - V_r) \\
&\qquad + 14.7[V_s - V_r - (A_r - A_s)]b_0 \approx V_ra_r + a_0(V_s - V_r) \\
C &= V_r(b_r - b_0 + a_ra_0 + 14.7a_rb_0 + 14.7b_ra_0) \\
&\qquad + V_sb_0 \approx V_r(b_r + a_ra_0) + b_0(V_s - V_r) \\
D &= V_r(b_ra_0 + b_0a_r + 14.7b_rb_0) \approx V_r(b_ra_0 + b_0a_r) \\
E &= V_rb_rb_0
\end{aligned} \tag{12}$$

From the experimental data on a GR-S stock the compressibility coefficients, a_r and b_r, were calculated by neglecting the third- and fourth-degree terms in Equation (11). From these coefficients the values of D and E and the resulting error in a_r and b_r were estimated. The error was much too small to be significant; consequently no terms in Equation (11) higher than the quadratic term need be considered.

We define the adiabatic compressibility coefficient by the equation:

$$\beta_S = -(1/V)(\partial V/\partial P)_S$$

The adiabatic volume of rubber is adequately represented by an equation of the form:

$$V = V_0[1 - a_r P - b_r P^2]$$

from which:

$$\beta_S = a_r + 2b_r P$$

EXPERIMENTAL RESULTS

Values of a_r and b_r for all the stocks investigated are given in Table I. The composition of these stocks are given in Table II. The error in a_r is

TABLE I

ADIABATIC COMPRESSIBILITY COEFFICIENTS

$V = V_0(1 - a_r P - b_r P^2)$, P = pressure in lb. per sq. in.

Stock	$a_r \times 10^6$	$-b_r \times 10^{10}$
I Hevea 100, S-8	3.51	0.8
II Hevea gum	3.28	—
III Hevea carbon black	2.83	0.3
III Hevea in above*	3.38	0.4
IV GR-S gum	3.36	0.8
V GR-S carbon black	2.67	0.2
V GR-S in above*	3.52	0.2
VII GR-I carbon black	2.79	0.15
VII GR-I in above*	3.38	0.2
VIII Hycar OR 15 gum	2.44	—
IX Perbunan gum	2.51	—

* Calculated from data for carbon black stock by correcting for compressibility of carbon black, assuming that the compressibility of carbon black was equal to that of graphite (3×10^{-6} atm.$^{-1}$, I.C.T.).

TABLE II

COMPOSITION OF COMPOUNDS

	I	II	III	IV	V	VI	VII	VIII	IX
Pale crepe	100	100	100						
GR-S				102	102				
GR-I						101.5	101.5		
Hycar OR-15								100	
Perbunan									100
Channel black			47		46		46		
Zinc oxide		5	8	5	5	5	5	5	5
Stearic acid		2	5	1.5	1.5	3	3	1	1.5
BLE		1	1						
AgeRite powder								1	
Captax		1	1	1.5	1.5				
Altax								1	1
XKA						1	1		
Sulfur	8	2.5	2.5	1.5	1.5	0.5	1.5	1	1.2
Cure (minutes)	180	43	37	37	55	37	55	37	20
Temperature (° C)	147	134	142	148	148	148	148	148	148

about 3 per cent, based on the standard deviation of the regression coefficient. However, since according to this estimate of error the compressibility of the rubber in a carbon black compound is not significantly different from the compressibility of the gum compound (Table I), this should be a valid estimate. The error in b_r ranges from about 3 per cent up, depending on the material. It was impossible to obtain some of the stocks in the form of rods free from air bubbles; e.g., gum stocks of Neoprene, Thiokol, and GR-I. The values of a_r for GR-I were calculated from the value obtained on a carbon black stock, after correcting for the amount of carbon black present.

Isothermal compressibilities were calculated from the adiabatic compressibilities by the equation[3]:

$$\beta_T = \beta_S + (T\alpha^2/C_p d)$$

where β_T = isothermal compressibility, β_S = adiabatic compressibility, T = temperature, α = volume coefficient of thermal expansion, C_p = heat capacity, and d = density. The values of the compressibilities and other properties necessary for the calculations are given in Table III.

TABLE III

SOME THERMODYNAMIC PROPERTIES OF ELASTOMERS

C_p = heat capacity, international joules per gram. α = volume thermal expansion (degree^{-1}) from measurements made in this laboratory by C. F. Eckert, W. R. Carlson, and E. M. Grabbe. β_S = adiabatic compressibility, dynes^{-1} cm.^{2} β_T = isothermal compressibility, dynes^{-1} cm.^{2}.

Compounds[4]	C_p	$\alpha \times 10^5$	$\beta_S \times \beta 0^{12}$	$\beta_T \times 10^{12}$	Density
I Hevea, 8 S			51	59	0.997
II Hevea gum	1.890	68	48	55	0.98
IV GR-S gum	1.905	64	49	55	1.00
VII GR-I	1.962	51	49	53	1.00
VIII Hycar OR 15 gum	1.970	59	35	39	1.04
IX Perbunan	1.97	59	36	40	1.02

The internal pressure of the elastomer may be calculated from the compressibility and coefficient of expansion, by the equation[5]:

$$P_i = T(\alpha/\beta_T)$$

Values of P_i for these stocks as well as values obtained for similar stocks by other workers are given in Table IV. P_i calculated from the thermodynamic properties is higher than P_i estimated from swelling experiments, although the comparative values between different polymers are roughly the same. The error in the isothermal compressibility and thermal expansion measurements is about 5 per cent, making the error in P_i approximately 7 per cent. The calculation of the numerical value of P_i from the coefficients of compressibility and thermal expansion requires the assumption that the change of internal energy of a system resulting from a change in volume at constant temperature is equal to the work done in overcoming the internal pressure. This assumption would appear to be valid for cases in which no transition between thermodynamic states of the system is involved. The assumptions underlying calculation of P_i from swelling data are more complex. It is assumed that maximum swelling is obtained in solvents with the same cohesive energy density (the cohesive energy density is equal to P_i). The cohesive energy densities of the solvents are obtained from their heats of vaporization. The assumptions involved here are such as to make P_i low[4]. For this reason, it would be ex-

TABLE IV

INTERNAL PRESSURE OF ELASTOMERS (CAL. CM.$^{-3}$) AT 298° K

Column 1 lists values calculated from compressibilities, determined in this work, and coefficients of expansion. Column 2 is calculated from published values of compressibility and coefficient of thermal expansion. Column 3 contains Scott, Burns, and Magat's values obtained from swelling (private communication). Column 4 lists Gee's values obtained from swelling[6].

Compound	P_i			
	1	2	3	4
Hevea, 8 S	83			
Hevea gum	88	85	70.0	63.7
GR-S gum[7]	83		73.1	65.5
GR-I	68			
Hycar OR-15 gum	108			
Perbunan	105			
Neoprene-GN			84.6	67.0
Buna-N			88.4	88.0
Polybutadiene			70.6	

pected that the values of P_i calculated from thermal expansion and compressibility measurements would be more reliable.

The internal pressures of rubber and GR-S are the same. GR-I has an internal pressure below that of rubber, while the internal pressures of Hycar OR and Perbunan are higher than that of rubber.

EFFECT OF ELONGATION ON THERMAL EXPANSION

In precise analysis of thermoelastic data of stretched elastomers, it is necessary to know how the thermal expansion and volume compressibility vary with elongation. A preliminary experiment was performed to determine the coefficient of thermal expansion of moderately stretched rubber. Samples of Hevea gum (II) were stretched to 100 per cent and 200 per cent elongation and tightly wrapped with Cellophane which was cemented in place. A turn of wire at each end of the wrapping kept it from splitting when the tension on the rubber was released.

The coefficient of thermal expansion, α, on these samples was determined in a dilatometer employing mercury or alcohol as the immersion liquid(Table V). The temperature range was −80 to 12° C.

TABLE V

THERMAL EXPANSION OF ELONGATED RUBBER

Per cent elongation	α
0	68×10^{-5} °C
100	67.5×10^{-5}
200	62.6×10^{-5}

At 100 per cent elongation α is the same within experimental error as it is at 0 per cent. At 200 per cent elongation there appears to be a significant decrease in α. This may be explained as due to partial crystallization of the sample. The appearance of a crystalline phase has two effects on the coefficient of expansion of rubber. The first effect is to decrease the coefficient of thermal expansion, since α for the crystalline phase is less than a third that of the liquid phase. The second effect is to raise the coefficient of expansion, since, in raising the temperature, part of the crystals melts and there is an

increase in volume due to the change in volume of rubber on melting. At room temperature and at those elongations where only a small amount of crystallization is produced, it may be that the first effect predominates.

These preliminary results suggest that at elongations not greater than 200 per cent, thermal expansion of elastomers is not much affected by elongation, but that larger effects may be expected at higher elongations if the polymer crystallizes. It seems reasonable to assume that similar remarks would apply to the compressibility.

SUMMARY

Adiabatic compressibility coefficients were measured on a series of cured polymers of commercial types under pressures up to 5000 pounds per square inch. In most cases, the second order as well as the first order coefficient could be determined from the data. The linear isothermal compressibility also was calculated from the measured linear adiabatic coefficient.

Preliminary measurements of the thermal expansion of a stretched Hevea gum stock show that there is a slight decrease in expansion at the 200 per cent elongation, presumably due to partial crystallization.

ACKNOWLEDGMENTS

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THE THERMODYNAMICS OF A STRAINED ELASTOMER. III. THE THERMAL COEFFICIENT OF MODULUS AND THE STATISTICAL THEORY OF ELASTICITY *

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INTRODUCTION

In the derivation of the equation of state of an elastomer by statistical mechanical methods, the assumption is made that the only effect of stretching a sample is to alter the possible number of configurations of the cross-linked network of flexible chain molecules. Then it follows that the resulting decrease in entropy is the only source of the observed retractive force, and the force is proportional to absolute temperature. To a first approximation the theoretical equations obtained agree with experimental data, both as to form of the stress-strain curve and as to the dependence of modulus on temperature.

However, significant departures from the theory occur. In the present paper the available thermoelastic data[1] have been analyzed statistically in an attempt to determine, as precisely as the data permit, what are the relative contributions of the two factors, entropy and energy, in developing the retractive force. Also, the variation of the entropy component of force with elongation is critically examined.

In carrying out this analysis, use is made of a stress-strain equation previously published by one of us[2].

THE STRESS–STRAIN EQUATION

The equation referred to has the form:

$$F = \frac{G}{2} (\lambda + 1) \left(1 - \frac{1}{\lambda^3} \right) + \frac{H}{2} (\lambda - 1) \left(1 - \frac{1}{\lambda^3} \right) \tag{1}$$

where F is the retractive force per unit initial area of a stretched elastomer, λ is the stretch, or $1 + e$ (e being the elongation), and G and H are the two moduli of superelasticity. This equation was derived from phenomenological considerations, on the assumptions:

(1) the rubber is isotropic and remains so in a plane normal to that of stretching
(2) the deformation occurs at constant volume
(3) the traction in simple shear in any isotropic plane is proportional to the shear.

It has been found that this equation fits experimental elongation stress-strain data fairly well up to the point of inflection[3].

Since all thermo-stress experiments have shown that the stress is a linear function of the temperature, it follows that the moduli G and H must be linear functions of temperature. Equation (1) can therefore be expressed in the more complete form:

$$F = a + bT = \tfrac{1}{2}G_0 P(\lambda) + \tfrac{1}{2}H_0 Q(\lambda) + \tfrac{1}{2}G_1 T P(\lambda) + \tfrac{1}{2}H_1 T Q(\lambda) \qquad (2)$$

where:

$$P = (\lambda + 1)(1 - 1/\lambda^3) \qquad \text{and} \qquad Q = (\lambda - 1)(1 - 1/\lambda^3)$$

Obviously, the stress intercept, a, and the slope, b, of a stress temperature curve can be expressed by the equations:

$$\begin{cases} a = (G_0/2)P(\lambda) + (H_0/2)Q(\lambda) \\ b = (G_1/2)P(\lambda) + (H_1/2)Q(\lambda) \end{cases} \qquad (3)$$

Calculations involved in fitting experimental data to the equation can be further simplified by rewriting Equations (3) in the form:

$$\begin{cases} a\lambda^3/(\lambda^3 - 1) = (G_0/2)(\lambda + 1) + (H_0/2)(\lambda - 1) = A + B\lambda \\ b\lambda^3/(\lambda^3 - 1) = (G_1/2)(\lambda + 1) + (H_1/2)(\lambda - 1) = C + D\lambda \end{cases} \qquad (4)$$

A large part of the published data was obtained by observing the stress as a function of the temperature while holding the sample at a constant length. An experiment conducted in this manner does not give directly or exactly the stress at constant deformation. If λ is to measure pure deformation; $i.e.$, change in shape, it must be defined as $\lambda = L/L_u$, where L is length and L_u is undeformed length at the same volume. Since L_u increases with temperature, L must also be increased with temperature if λ is to be kept constant.

This matter has been analyzed in the first paper[4] of the present series, where it is shown that general superelastic functions, of which Equation (1) is an example, are still valid when assumption (2) above is only approximately valid. As part of this analysis, an equation was derived for calculating stress at constant λ from observed stress at constant L. In our present notation and with sufficient approximation, this equation is:

$$F(\lambda, T) = F(L, T) - (\beta/3)(T - T_0)L(\partial F/\partial L) \qquad (5)$$

We have ignored here the volume changes resulting from changes in mean pressure acting on the bulk compressibility, but calculations show that, in the experiments to be analyzed, such volume changes are negligible.

A check on the equivalence of the two experimental procedures ($i.e.$, observing the stress as a function of the temperature at constant elongation or, in the second method, at constant length) is provided by the data on GR-S obtained by Roth and Wood[5].

The results obtained by the two methods are illustrated in Figure 1, where a portion of the stress-strain curves at $0°$ is plotted in the neighborhood of $\lambda = 1.5$. The solid curve is a stress-strain curve obtained by plotting the stress temperature data at a constant elongation. The dashed curve is the stress-strain curve obtained from the data observed at constant length, after correcting, by Equation (5), for the effect of the change in temperature on the elongation. It is seen that the stress corrected to constant elongation lies above the stress observed at constant elongation.
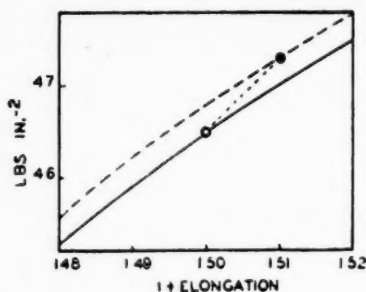
Fig. 1.—The solid curve is a portion of the stress-strain curve obtained from data observed at constant elongations; the dashed curve was obtained from observations at constant length by correcting for the temperature change.

One explanation for the discrepancy described here may be that the temperature cycle involved in the experiment where the length of the sample is held constant produces a small elongation cycle, and that the slope of the line joining the corrected stress and the observed stress corresponds to the dynamic modulus of the stock in such a small cycle rather than to the local slope of the over-all stress-strain curve. The latter slope was the only one derivable from published thermoelasticity data; but Wiegand and Snyder[11] have shown that the modulus of elasticity in a short cycle of elongation about a mean value different from zero is much larger than the modulus obtained from the equilibrium stress-strain curve. In view of this work, it is felt that, if it is possible to apply thermodynamic methods to this system at all, the correct modulus for use in Equation (5) is the one obtained by executing an elongation cycle comparable in amplitude to the cycle produced by the temperature changes. The discrepancy shown in Figure 1 is in the direction to be expected on the basis of this discussion.

ANALYSIS OF THERMOELASTICITY DATA

Since the discrepancy between the observed and calculated curve is small, it was ignored and the value of the coefficients in Equation (2) were calculated from the experimental data after being corrected by Equation (5) for the effect of temperature upon the elongation. The coefficients are given in Table I.

The entropy contribution to the stress is:

$$T(\partial F/\partial T) = \tfrac{1}{2}G_1 TP(\lambda) + \tfrac{1}{2}H_1 TQ(\lambda) \tag{6}$$

TABLE I

VALUES OF COEFFICIENTS IN EQUATION (2)

Units of values in parenthesis are lbs. per sq. in. for G_0 and H_0, lbs. per sq. in. degree^{-1} for G_1 and H_1. All other values are in g. per cm.$^{-2}$ and g. per cm.$^{-2}$ degree^{-1}.

Compound	$\tfrac{1}{2}G_0$	$\tfrac{1}{2}G_1$	$\tfrac{1}{2}H_0$	$\tfrac{1}{2}H_1$
1. Hevea-commercial gum[2]	1030	4.5	-1860	6.2
2. Hevea 100-S8[6]	900	5.0	-2640	6.6
3. Hevea gum[7]	385	7.4	-1180	5.2
	(5.5)	(0.10)	(-16.8)	(0.074)
4. GR-S gum[8]	-343	8.0	-245	1.9
	(-4.9)	(0.11)	(-3.5)	(0.027)
5. Hycar[9]	150	4.8	-9510	24.
6. Neoprene[10]	2390	0.7	-8470	39.
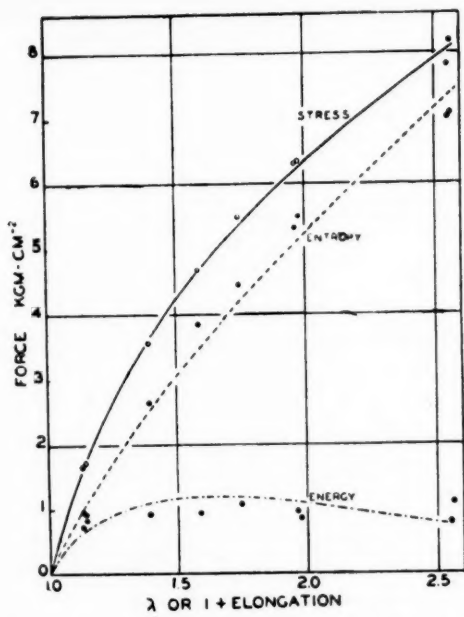
FIG. 2.—Hevea, compound 1, commercial stock hardess 40.
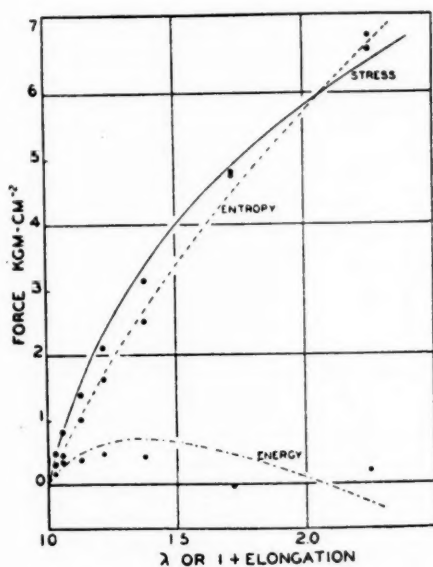
FIG. 3.—Hevea, compound 2, 100 rubber—8 sulfur.
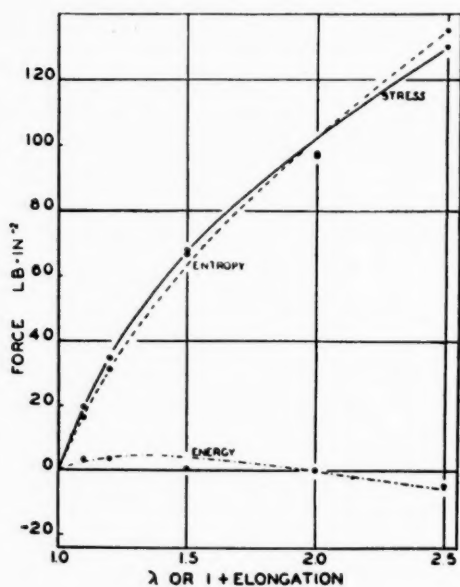
Fig. 4.—Hevea, compound 3.
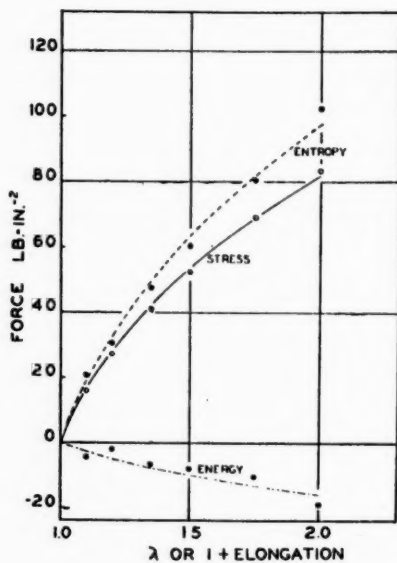
Fig. 5.—GR-S, compound 4.
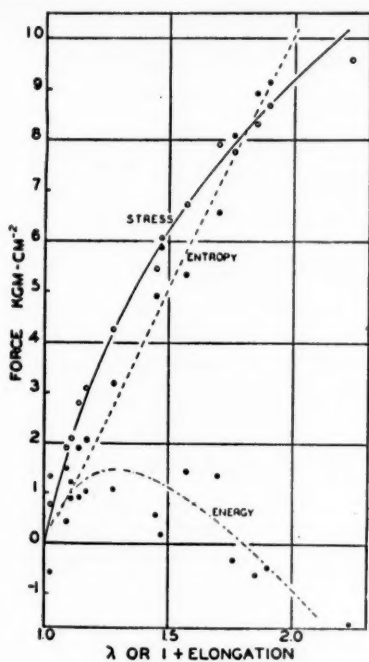
FIG. 6.—Hycar, compound 5.
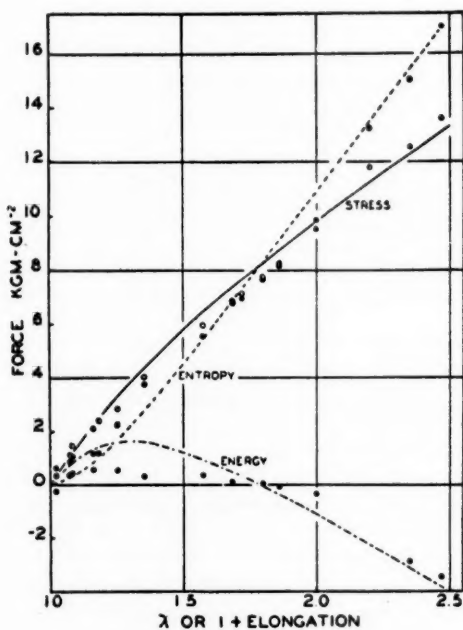
FIG. 7.—Neoprene, compound 6.

The energy contribution to the stress is:

$$F - T(\partial F/\partial T) = \tfrac{1}{2}G_0 P(\lambda) + \tfrac{1}{2}H_0 Q(\lambda) \tag{7}$$

The curves obtained at a single temperature with these coefficients are plotted in Figures 2–7. The three points at a given elongation show the total (observed) stress, the slope multiplied by the absolute temperature or the entropy part of the stress, and the intercept on the stress axis or the energy part of the stress. The constants of A, B, C, and D in Equation (4) were fitted to the data by the method of least squares. The agreement between the calculated curves and the observed data is fairly good.

TESTS OF STATISTICAL MECHANICAL THEORY OF ELASTICITY

The coefficients of Equation (2) provide two tests for the statistical theory of elasticity. The fundamental assumption of the statistical theory is that the entropy change is responsible for the stress. If this is true, then:

$$- \lim_{\lambda \to 1} \left[(\partial S/\partial \lambda)_{T,P}/F \right] \equiv \left[G_1 T/(G_0 + G_1 T) \right] = 1 \tag{8}$$

Wall[12] observed that the statistical theory predicted that H would be equal to G in Mooney's equation. Since the statistical method considers only the entropy of deformation, we take the prediction to mean:

$$H_1/G_1 = 1 \tag{9}$$

These two predictions can be tested with the values of the moduli listed in Table I. Results are shown in Table II.

TABLE II
RATIOS AND THEIR SIGNIFICANCE

By the statistical theory, $H_1/G_1 = G_1 T/(G_0 + G_1 T) = 1$. P is the probability that the observed value in the preceding column differs from 1 because of chance errors.

Compound	H_1/G_1, or α		P	$G_1 T/(G_0 + G_1 T)$		P
1. Hevea-commercial gum[2]	1.37	±0.58	>0.5	0.57	±0.05	<0.001
2. Hevea 100-S8[6]	1.32	±0.38	>0.5	0.63	±0.04	<0.001
3. Hevea gum[7]	0.71	±0.18	0.22	0.85	±0.03	0.018
4. GR-S gum[8]	0.24	±0.13	0.005	1.18	±0.09	0.10
5. Hycar[9]	5.26	±2.8	0.14	0.28	±0.10	<0.001
6. Neoprene[10]	60	±265	>0.5	0.77	±0.33	<0.05

Variance analyses have been made to determine if the deviations from unity of the two ratios of Equations (8) and (9) are significant. This was done by computing the variances for the independent coefficients A, B, C, and D in Equation (4). From these variances, the variance of each ratio was calculated by the theory of propagation of errors. Values of the ratios, their standard deviations, and an estimate of their significance is given in Table II. Columns 2 and 4 in Table II give the probability, obtained by applying Student's t test, that the departure of the observed ratio from unity is due to chance errors. A probability of 0.05 indicates that the difference between the observed ratio and unity is significant. A probability less than 0.01 is an indication that the difference is highly significant. It is to be remembered that variance analysis deals only with chance errors; systematic errors are beyond its power.

CONCLUSIONS DERIVED FROM THE STATISTICAL ANALYSIS

A. HEVEA GUM COMPOUNDS

For all the Hevea compounds[13], Figures 2–4, the ratio H_1/G_1 is not significantly different from unity. Hence the equation of state derived from the statistical theory adequately represents the entropy contribution to the stress. The ratio $G_1T/(G_0 + G_1T)$ is significantly different from unity. Hence the energy change makes a significant contribution to the stress at low elongations. The fact that the internal energy first increases, then decreases rapidly, suggests that there may be two mechanisms by which the energy changes with elongation. The decrease in energy can be attributed to crystallization induced by high stretch, but the cause of the initial rise in energy is not obvious.

B. GR-S

For the one GR-S compound reported, Figure 5, the ratio $G_1T/(G_0 + G_1T)$ is not significantly different from one, showing that the entropy contribution is practically the whole stress. On the other hand, H_1/G_1 is significantly and considerably different from one; hence in this case the statistical equation of state does not represent even approximately the form of the entropy-elongation curve. Since, by x-ray analysis, GR-S does not crystallize appreciably, the negative energy component of stress is unexpected and, so far, unexplained.

C. HYCAR AND NEOPRENE

The scattering of the data, Figures 6 and 7, for these two stocks at low elongations is large, and the precision of the ratio H_1/G_1 is very low. However, the statistical equation fits the data within their experimental error. The ratio $G_1T/(G_0 + G_1T)$ is significantly different from one in both cases, showing that the energy contributions are significant.

THERMOELASTIC EFFECTS FROM TWISTING
COUPLE MEASUREMENTS

Recently in this laboratory a series of experiments was performed to determine with high precision the thermoelasticity effects at very small deformations. The need for such measurements arises from two facts: (1) the statistical theory of elasticity ignores crystallization effects and hence is valid only for low elongations before crystallization or any other phase change is induced by the elongation, and (2) current methods of measuring thermoelasticity in elongation are relatively inaccurate at low elongations.

The specimen, a cured gum stock, was in the form of a rectangular rod, approximately $\frac{1}{10} \times \frac{1}{10} \times 3$ in. It was first held twisted 1 revolution for 15 minutes in a Dewar flask of water at 70° C to permit relaxation to an approximately steady value of the twisting couple. The temperature was then changed repeatedly from 2° to 50° C and back, while the twisting couple of the sample was measured by means of an opposing steel suspension ribbon. The sample is permitted to expand freely in the longitudinal as well as lateral direction, and consequently the extent of the shearing deformation in any element of the sample is unaltered by thermal expansion.

The relative coefficient of thermoelasticity calculated from the measurements is:

$$J = (\Delta C/C)(T/\Delta T)$$

where C is the twisting couple and T is absolute temperature. If the stress results entirely from entropy, $J = 1$; and if it is found experimentally that $J = 1 + j$, then $-j$ is the fractional contribution to the total stress arising from internal energy change. The value of J has been determined for nine different polymers. The data are presented in Table III. J is approximately

<div align="center">

TABLE III

RELATIVE COEFFICIENT OF THERMOELASTICITY

</div>

Compound	$J = (\Delta C/C)(T/\Delta T)$
Hevea gum (6 compounds)	0.96–1.00
GR-S (2 compounds)	1.18*
Hycar OR-15	1.16*
Neoprene GN	1.01
Polymethylpentadiene	1.15*
Polyisoprene	1.21*
Perbunan	1.16*
Butyl	1.04
Thiokol-FA	1.04

* Significantly different from 1 at the 5 per cent level.

1 in all cases; the small departures from 1.0 are significant in five cases. In all cases where there is a significant departure from 1, $j > 0$, and the internal energy decreases with deformation.

The agreement between the two methods of determining the entropy contribution to the stress is not good. However, the experimental evidence indicates that the torsional test is the more reliable of the two, and the results obtained with it give stronger support to the statistical theory of elasticity than can be found in measurements with the elongation method.

While these data thus conform approximately to the prediction that the stress is proportional to the absolute temperature, we can infer nothing from these results regarding the predicted relationship between the factor of proportionality and the molecular structure of the material.

It is to be observed that in this analysis we have accepted the usual assumption that the experimental technique in this field is adequate to yield essentially true equilibrium stress-strain curves. This assumption may be questionable.

Gee[4] shows that if a loaded sample is swelled with a volatile liquid and then deswelled, the stable length is increased. With the swelling technique, Gee finds that force at a given λ is proportional to the absolute temperature within experimental error; but the stress-strain curves do not follow the kinetic theoretical relationship, $f = G(\lambda - 1/\lambda^3)$. It is possible to calculate α from the form of Gee's curves (for the dry stocks), and it is found that $\alpha \lesseqqgtr .1$ for Hevea, Buna-N, Thiokol, Neoprene-GN, and GR-S. These results are definitely in disagreement with the statistically significant values of α in Table II of the present paper. It is possible, that these differences in α are due to differences in compounding and curing; but it seems much more probable that they are due to differences in experimental procedures.

The outstanding conclusion from this critical work is that experimental techniques in this field need improvement. Even the extremely laborious swelling and deswelling technique may not give true equilibrium curves, as Gee himself rightly points out.

In spite of imperfections of method, it now seems definitely established that the force at a given deformation is closely, but probably not exactly, propor-

tional to absolute temperature. But there is still considerable doubt concerning α and the precise form of the stress-strain curve; and whether the statistical theory of elasticity is correct in this respect remains an open question. In deciding this question, stress-strain curves in both elongation and compression of the same samples would probably be helpful.

SUMMARY

Published thermoelasticity data are critically analyzed by means of thermodynamic equations developed in the first paper of this series. Equations known to be of the proper form are fitted by least squares to the experimental data, which were first corrected to allow for the changes in shape when tested under variable temperature and constant length. If the measurements are accepted as truly reversible, the data show that several different elastomers depart considerably in some respects from the predictions of the statistical theory of elasticity.

Some thermoelasticity measurements in torsion are reported which seem to give the most reliable evidence that stress is proportional to absolute temperature.

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THE FORMATION AND STRUCTURE OF VULCANIZATES *

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The characteristic mechanical properties of vulcanized rubber are believed to result from a network structure made up of chainlike molecules bonded together by occasional cross-linkages. In relating the physical properties of the vulcanizate to the structure of the network, it is therefore necessary to consider the concentration of cross-linkages and the molecular-weight distribution of the rubber molecules before cross-linking. Various theories have been proposed for the dependence of elastic properties on these structural factors, but experimental proof of the suggested relations has been meager, largely because of the complexities met with in vulcanization reactions. In the present investigation some of these difficulties have been overcome, and the quantitative relations between the elastic behavior of GR-S and its network structure have thereby been revealed.

THEORETICAL CONSIDERATIONS

ELASTICITY

Of the many theories that have been proposed to account for rubberlike elasticity, the most explicit are those which consider the configurations of coiling molecules. The equation of state for systems of flexible chains has been expressed[1] in the form:

$$\tau = \frac{\nu}{V} RT \left(\frac{l}{l_0} - \frac{l_0^2}{l^2} \right) \tag{1}$$

τ = tension (force per unit area of initial cross-section)
R = gas constant
T = absolute temperature
l = stretched length
l_0 = unstretched length

ν/V is a proportionality constant which represents the rigidity of the particular rubber sample and depends on the structure. Several authors[2] have interpreted ν as the number of chains in volume V, but here ν/V will be regarded as an experimental quantity and will henceforth be called the *network activity*.

The dependence of tension on temperature and elongation expressed by Equation 1 agrees fairly well with experimental thermoelastic properties[3] and stress-strain curves[4] for various rubberlike polymers. It is with the dependence of the remaining term, ν/V, on network structure that we are here chiefly concerned. In several elasticity theories this quantity is proportional to the

number of chains per unit volume, where the chain is defined as the part of a molecule extending from one cross-linkage to the next.   For an ideal network formed from indefinitely long molecules the number of chains is identical with the number of cross-linked monomer units or equal to twice the number of cross-linkages.   If a fraction ρ of the structural units is involved in cross-linkages, the concentration of chains (moles per cc.) is $(d/M_0)\rho$, and the theoretical relation between network activity and degree of cross-linking, ρ, is given by:

$$\frac{\nu}{V} = g\,\frac{d}{M_0}\,\rho \tag{2}$$

d = density of polymer (g. per cc.)
M_0 = molecular weight of the structural unit.

The proportionality constant, g, is unity in the theories developed by Wall[5], Treloar[6], and Flory and Rehner[7].   It has the value 7/3 in the theory of Kuhn[8] and about $\frac{1}{2}$ in that of James and Guth[9].

Flory has taken into account the molecular weight of the polymer before cross-linking[10].   Each primary molecule is considered to give rise to two inactive terminal chains in the vulcanizate, thereby leading to an effective degree of cross-linking of $\rho(2/\bar{y}_n)$ where $\bar{y}_n$ is the number average degree of polymerization prior to cross-linking.   Equation 2 may then be modified to

$$\frac{\nu}{V} = g\,\frac{d}{M_0}\left(\rho - \frac{2}{\bar{y}_n}\right) \tag{3}$$

This equation, which relates the modulus of vulcanized rubber to the network structure, as determined by the degree of cross-linking and the primary molecular weight, has hitherto received only partial experimental verification.   Experiments by Flory with close-cut fractions of Butyl rubber confirmed the validity of the correction for initial molecular weight, but failed to support the theoretical proportionality between network activity and degree of cross-linking[10].   Experimental values of g were 3.3 for $\rho = 1.6 \times 10^{-3}$ and 2.1 for $\rho = 2.8 \times 10^{-3}$.   Flory has suggested that the discrepancy between theory and experiment results from the presence of entanglements within the network.

SWELLING

Although the network activity is generally estimated from modulus measurements, it may also be determined from observation of the equilibrium swelling volume[11].   The relation is given by:

$$\frac{\nu}{V} = \frac{\ln(1 - v_2) + v_2 + \mu_\theta v_2^2}{-V_1 v_2^{\frac{1}{3}}} \tag{4}$$

v_2 = volume fraction of polymer in the swollen gel in equilibrium with pure solvent, i.e., the reciprocal of the swelling volume (ratio of the volumes of swollen and dried gel).

μ_θ = solvent-plymer interaction coefficient[12].
V_1 = molar volume of solvent.

For large swelling (v_2 small) Equation 4 reduces to the approximate expression:

$$\frac{\nu}{V} = \frac{(1 - 2\mu_\theta)v_2^{5/3}}{2V_1} \tag{5}$$

PRIMARY MOLECULAR-WEIGHT DISTRIBUTION

The primary molecule is defined as the polymeric molecule that exists before cross-linking and therefore constitutes a basic factor in vulcanizate structure. The size distribution of the primary molecules is the statistical result of the random occurrence of termination steps during chain growth. If the probability that a growing molecule adds an additional monomer unit is represented by p, then the distribution of primary molecular size of the resulting polymer[13] is given by:

$$W_y = y(1 - p)^2 p^{y-1} \tag{6}$$

W_y = weight fraction of species containing y structural units.

For this distribution, the weight average degree of polymerization, $\bar{y}_w$, is twice the number average, $\bar{y}_n$; i.e., the heterogeneity index is two[13].

With polymers formed in the presence of a chain transfer agent (modifier), the number average degree of polymerization of the primary molecules may be obtained from measurements of modifier consumption, viz.:

$$\bar{y}_n = \frac{\alpha}{R_0(1 - \epsilon^{-r\alpha})} \tag{7}$$

α = fractional conversion

R_0 = modifier concentration (as moles per mole of initial monomer)

r = regulating index[14].

Depletion of modifier during polymerization broadens the primary molecular-weight distribution somewhat; the primary heterogeneity index at conversion α is given [15] by:

$$\frac{y_u}{y_n} = \frac{1}{(r\alpha)^2} (\epsilon^{r\alpha} - 1)(1 - \epsilon^{-r\alpha}) \tag{8}$$

NETWORK FORMATION

During vulcanization, long chains of a rubberlike polymer are bonded together at randomly selected points, and larger and larger structures are thereby built up. As the process of interlinking continues, a point is reached where
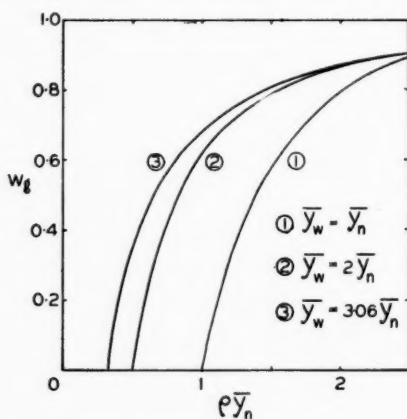
FIG. 1.—Statistical relation between weight fraction of gel, W_g, and average number of cross-linked units per primary molecule, ρY_n, for (1) homogeneous polymer, (2) increment, and (3) cumulative distributions.

infinite networks pervading the entire volume suddenly appear[16]. Such networks are insoluble, and constitute the familiar gel fraction. Further cross-linking results in increasing amounts of gel and in cyclic connections within the gel structure.

On the assumption that cross-linking is random and that intramolecular connections within the sol fraction may be neglected, Flory[17] and Stockmayer[18] have developed a statistical treatment of the cross-linking process. Figure 1 shows the theoretical course of gelation as a function of the average number of crosslinked units per primary molecule ($\rho \bar{y}_n$) for three cases, viz., the homogeneous polymer, the increment distribution (Equation 6), and the cumulative distribution resulting from 90 per cent depletion of modifier[15]. The latter corresponds to a heterogeneity index of 3.06.

As cross-linking proceeds beyond the gel point, cyclic connections form within the gel structure. Only these connections give rise to effective chains. The number of such effective chains per primary molecule is given by $\bar{y}_n[\rho'' - (2/\bar{y}_n'')]$ where ρ'' and $\bar{y}_n''$ are the value of ρ and y_n in the gel. Figure 2 shows the theoretical number of effective chains per primary molecule
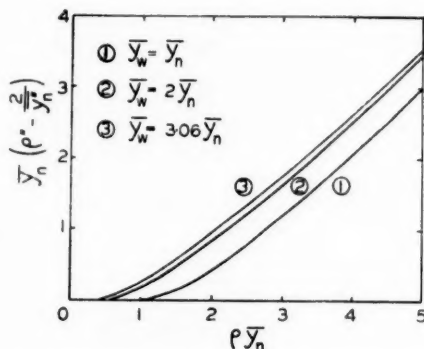
Fig. 2.—Statistical relation between the number of effective chains and the average number of cross-linked units per primary molecule for (1) homogeneous polymer, (2) increment, and (3) cumulative distributions.

for the same three distributions. The curves shown in Figures 1 and 2 were calculated by the method proposed by Flory[19].

EXPERIMENTAL DETAILS

PREPARATION OF POLYMERS

The copolymer of butadiene and styrene (GR-S) was prepared by the well-known bottle polymerization method[20]. After addition of shortstop to the latex, unreacted monomer was removed by vacuum distillation at about 40° C. The molecular weight of the polymer was varied by manipulation of the amount of modifier used (Sharples tertiary dodecanethiol). The regulating index of this modifier[14] is 3.16. The degree of polymerization of the primary molecules was calculated by means of Equation 7; due allowance was made for compositional changes during polymerization[21]. The heterogeneity index was calculated by means of Equation 8, and is shown in Table 1, together with other relevant characteristics of the polymers.

TABLE 1

DEGREE OF POLYMERIZATION AND HETEROGENEITY INDEX OF
MODIFIED GR-S POLYMERS

Polymer no.	Thiol charged (moles per mole of initial monomer) R_0	Conversion α	Number average degree of polymerization y_n	Heterogeneity index $\dfrac{y_w}{y_n}$
I	0.44	0.304	11,600	2.16
II	1.42	0.232	3,150	2.09
III	2.95	0.465	2,080	2.38
IV	4.47	0.107	870	2.02
V	4.47	0.275	1,100	2.13
VI	4.47	0.356	1,220	2.22
VII	7.37	0.171	575	2.05
VIII	14.2	0.136	275	2.03
IX	58.9	0.515	110	2.52

CROSS-LINKING REACTION

A buffered solution of potassium persulfate was added to the latex; the final mixture had the composition:

Polymer (GR-S)	5.0%
Potassium persulfate	2.5%
Buffer (sodium carbonate-sodium bicarbonate)	1.5%

After thorough mixing, aliquots amounting to 25 cc. were transferred to one-ounce bottles. Nitrogen was bubbled through the reaction mixture for 30 seconds, after which the bottle was capped tightly and immersed in a water bath at $50 \pm 0.5°$ C. After suitable intervals the reaction was stopped by coagulating the polymer in rapidly stirring butanol containing 0.05 per cent phenyl-betanaphthylamine antioxidant (P.B.N.A.). The coagulum was washed with butanol; 2 per cent of P.B.N.A. was added, and the polymer was dried for 12 hours at 80° C in a vacuum oven.

To compare the cross-linking reaction brought about by potassium persulfate with more conventional vulcanizations, one of the polymers was mixed with compounding ingredients and cured at 140° C. The curing ingredients were added in the form of a colloidal dispersion to the latex, which was then coagulated in butanol. The coagulum was protected with P.B.N.A. and milled for a short time at room temperature; the roll separation was one millimeter. Portions of the coagulum were then cured at 140° C.

SOLUBILITY AND SWELLING

Weighed fragments of the dried polymer were placed in small screen cages and extracted for 48 hours in toluene containing 0.05 per cent of P.B.N.A. The swollen gel was allowed to drain for five minutes in a small closed container, weighed, and then dried to constant weight. The gel fraction and swelling volume were calculated, using the values of 0.93 and 0.86 for the densities of GR-S and toluene, respectively. The solubility was corrected for the small amount of nonpolymer components extractable in ethanol-toluene azeotrope containing 10 per cent water[22].

RESULTS AND DISCUSSION

CROSS-LINKING

The addition of potassium persulfate to GR-S latex results in progressive insolubilization of the polymer (Figure 3). The course of gelation is seen to
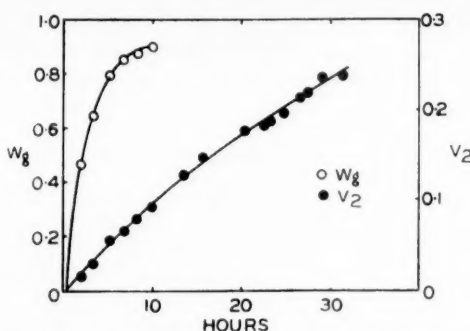
Fig. 3.—Rate of increase of gel fraction, W_g, and reciprocal swelling volume V_2, with time.

resemble closely the theoretical curve (Figure 1) for the increase of gel fraction as cross-linkages are added.   One may therefore employ the theoretical relation with confidence to deduce the degree of cross-linking from the measured gel fraction.

THE RELATION OF SWELLING TO MODULUS

On comparing Equations 1 and 5, it is seen that the modulus of a vulcanizate is predicted to be approximately inversely proportional to the 5/3 power of the swelling volume.   Measurements on GR-S pure-gum vulcanizates amply confirm this relation (Figure 4).

Stress-strain curves were determined with a standard testing machine; the rate of extension was 20 inches a minute.   In addition to the dynamic modulus determined in this way, the static modulus was estimated by subtracting the stress relaxation occurring during a period of 24 hours.

Figure 4 consists of a log-log plot of the dynamic and static moduli at 300 per cent elongation (τ_{300}) vs. the swelling volume in toluene (S.V.).   Although both dynamic and static moduli show good correlation with the swelling volume, better agreement with theory is found for the static modulus.   The result is not surprising, since swelling volume represents an equilibrium type of deformation. The equation of the line in Figure 4 for the static modulus is:

$$\log \tau_{300} = 3.67 - 1.67 \log \text{S.V.}$$
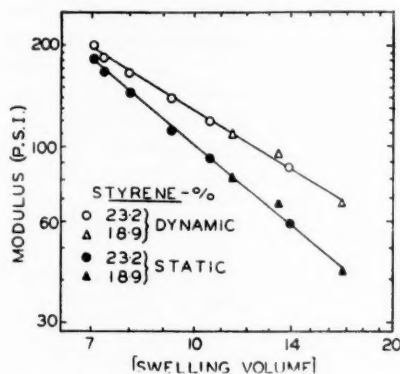
Fig. 4.—Modulus at 300% elongation vs. swelling volume (log-log plot).

The theoretical slope of $(-5/3)$ is seen to be confirmed. By comparing the above equation with Equations 1 and 4, the value of μ_g is found to be 0.18 for GR-S in toluene. Small variations of styrene content do not appear to alter this value significantly.

SWELLING AND NETWORK STRUCTURE

It is evident from Figure 3 that large changes of swelling volume occur when the degree of cross-linking is altered. Marked dependence of swelling on primary molecular weight was also found when the various polymers listed in Table 1 were cross-linked by the same method. The dependence of swelling on network structure is best discussed in terms of the theoretical predictions summarized in Equation 3. For this purpose the value of ρ, the degree of cross-linking was calculated from the measured gel fraction with the assistance of Figure 1. The network activity ν/V was calculated from the observed swelling volume by means of Equation 4, using the value 0.18 for μ_g.

Figure 5 shows the effect of both primary molecular weight and degree of cross-linking on the network activity (modulus) of GR-S. The effect of primary molecular weight is particularly noteworthy. Polymers of low primary
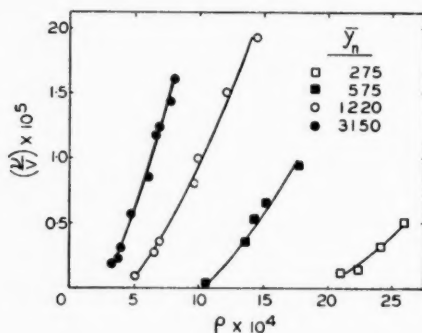
FIG. 5.—Network activity vs. degree of cross-linking.

molecular weight are handicapped in the development of reversible elasticity because relatively large concentrations of cross-linkages are required for the formation of a network. Even after the gel point is reached, the increase of modulus is less rapid than with polymers of high primary molecular weight.

It is of interest to test the extent to which the results shown in Figure 5 agree with Flory's postulate that terminal chains are inactive during deformation. Accordingly, the effective degree of cross-linking $\rho'' - 2/\bar{y}_n''$ for the various cross-linked polymers was deduced with the assistance of Figure 2. Consideration of the molecular weight in this way is seen to bring all the results into agreement (Figure 6). Thus the effect of molecular weight over a hundred-fold range is in quantitative agreement with the network flaw theory of vulcanizate structure[23].

The linearity of the resulting plot also verifies the proportionality between network activity and (effective) degree of cross-linking predicated by various elasticity theories. The equation of the line in Figure 6 is:

$$\frac{\nu}{V} = 0.039 \left(\rho'' - \frac{2}{\bar{y}_n''} \right)$$
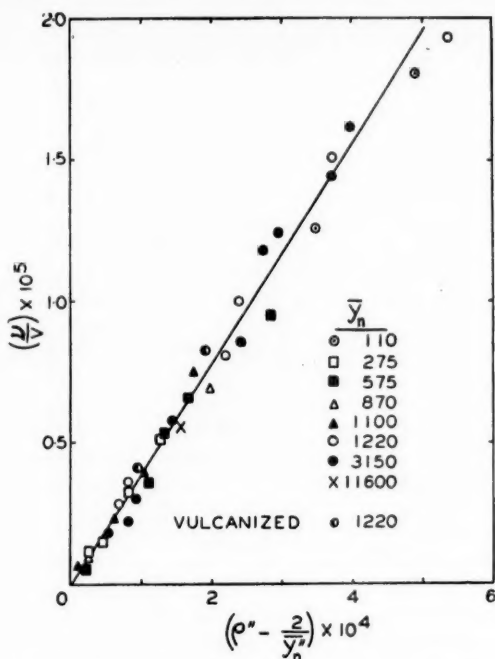
Fig. 6.—Network activity vs. effective degree of cross-linking.

Substituting $d = 0.93$, $M_0 = 59.2$, and comparing with Equation 3, the value of g is found to be 2.5, in good agreement with the value of 7/3 predicted by Kuhn.

Figure 6 also includes the results deduced from the swelling and solubility of GR-S pure-gum vulcanizates at low degrees of cure.   The coincidence of the
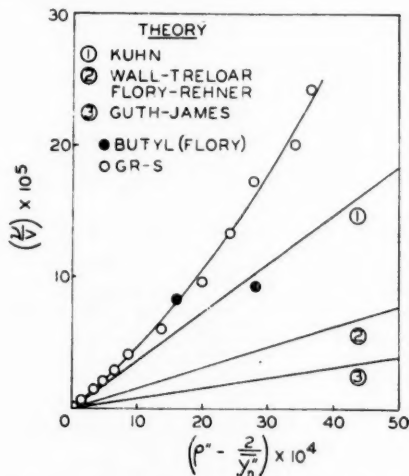
Fig. 7.—Network activity vs. effective degree of cross-linking.   Comparison of experimental results for GR-S and for Butyl (Flory) with elasticity theories.

results demonstrates that the above conclusions concerning the effects of network structure are equally applicable to GR-S vulcanizates.

The effect of much higher concentrations of cross-linkages on the network activity was investigated by extending the reaction period with one of the polymers (III).   The degree of cross-linking was calculated from the measured rate of insolubilization early in the reaction; due allowance was made for decomposition of persulfate ion.   The results, shown in Figure 7, indicate that in this region the rigidity increases more rapidly than the effective degree of cross-linking.   Included in Figure 7 are Flory's results for Butyl rubber ($g = 3.3$ and 2.1) and the predictions of elasticity theories.   Of the various theories, that of Kuhn appears to be in closest agreement with the experimental results for GR-S except at high degrees of cure.   Kuhn's hypothesis (5) that restraints in addition to chemical cross-linkages exist along the chains appears to be correct.

The most significant feature of these results is the way in which molecular weight exerts its effect on elastic properties.   The ends of each primary molecule give rise to flaws in the network structure which are deterimental to physical properties[24].   Consideration of the relatively low value of the primary molecular weight of GR-S, as now produced, leads to the conclusion that such flaws make up a considerable fraction of the structure of typical vulcanizates.

The effect of distribution of primary molecular weight may be discussed on the basis of Figure 2.   For a given number average primary molecular weight a fixed degree of cross-linking results in a slightly greater fraction of effective chains with the more heterogeneous polymer.   This advantage of heterogeneity is small, and may easily be illusory when processing difficulties are considered.

ACKNOWLEDGMENT

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CREEP, RECOVERY, AND PERMANENT SET FOR GR-S AND HEVEA *

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Creep, the slow progressive deformation or flow which occurs under stress for a great many materials, is especially prominent in elastomers. But creep also presents technical problems in the use of metals at high temperatures, and has been observed in nature on a grand scale for ice and rocks and in the laboratory for glass and all sorts of high polymers, including natural and synthetic textiles, rubbers, and plastics. Against this background of information, the fact emerges that many aspects of creep phenomena are very much the same wherever they are observed. Since the time of Maxwell, creep has been thought of and described in terms of ideal molecular mechanical models consisting of springs and dashpots[1]. These models have sufficed to explain the general character of the results, but calculations become unwieldy and of limited significance for systems with unspecified molecular units of flow and distributions of relaxation times. Because of the variety of types of molecular structures in which creep occurs, it is apparent that any molecular theory must be on a very broad basis. Since creep phenomena in diversified materials are so similar, it is to be expected that definite and convincing deductions from experimental curves in regard to the molecular structure and flow units and mechanisms of flow will be difficult. The reaction rate concepts of molecular flow developed by Eyring are sufficiently general to be used for molecular theories of creep[2]. In applying the theory to a network molecular structure[3], Tobolsky and Eyring assumed that the primary network units did not break and that segment motion could be neglected. The flow under constant stress because of breaking or slipping of secondary bonds was deduced to obey an equation of the form:

$$S = a + b \log t \tag{1}$$

where S is the strain and a and b are parameters, the values of which depend on the temperature and the molecular magnitudes used in the theory. The theory does not apply directly to creep recovery, which is activated by internal molecular forces.

Although the deductions from this molecular theory of creep conform in a general way to the observations, there is much to be desired in regard to specificity as to the types of bonds, bond strengths, or activation energies and units of flow involved. It is doubtful if the molecular constants, which must be deduced from experimental creep results, are really constant for a very wide range of experimental conditions. These difficulties may be inherent in the character of molecular network structures, since it is reasonable to suppose that a distribution of secondary bond strengths exists; hence confusion may

arise in trying to distinguish between effects from strong secondary bonds and primary bonds. Likewise there may be an indefiniteness in the size of the units of flow.

Andrews, Tobolsky, and Hanson[4] have proposed a molecular theory of permanent set for rubber during relaxation at elevated temperatures which assumes that new network chains are formed during relaxation. These new chains are at equilibrium in the stretched condition. They are considered, therefore, to resist retraction when the load is removed. The general ideas would be applicable for any permanent set which occurs during a creep test, but it is doubtful if many new primary bonds of the type contemplated are formed at more moderate temperatures. Hence it is desirable to explain the permanent set observed after creep tests such as will be described on the basis of some irreversible flow mechanism, without using the idea of new primary bond formation.

The experiments reported here were undertaken with the idea that additional information on creep and flow processes, and hence molecular structure for GR-S and other rubbers, might be obtained by measuring creep for a range of elongations and cures and correlating the results with the corresponding observations of creep recovery and permanent set. In the case of Hevea, creep phenomena at higher elongations are complicated by the occurrence of progressive crystallization during the tests[5]. Comparison with GR-S should be instructive for studying this effect.

The occurrence of creep is one of the fundamental limitations of elastomers in many applications, so a better understanding of how it comes about may have technical importance as well as significance for the general knowledge and theory of the molecular structure of elastomers. Creep is a manifestation of imperfect elasticity which, under other circumstances, may become evident as stress relaxation and hysteresis. A review of creep studies, from the engineering standpoint, has been given in a recent British publication[6]. The general mathematical relationships between creep and relaxation based on the superposition principle and linear mechanical models have been recently presented by Gross[7].

METHODS OF DESIGNATING CREEP

In engineering usage, creep in rubber is usually defined as the percentage change in elongation, compression, or shear in any specified time. Figure 1 represents a plot of the gauged length of a test-piece against the time. The initial elongation is $100(l_s - l_0)/l_0$. The elongation at time t is $100(l_t - l_0)/l_0$.
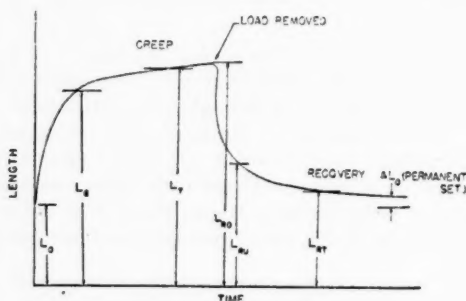
Fig. 1.—Diagram of deformations in creep and recovery processes.

The increase in elongation is $100(l_t - l_s)/l_0$. The percentage increase in elongation is $100(l_t - l_s)/(l_s - l_0)$. This is usually used as a measure of the creep. One of the ideas behind this definition is to secure a result which is relatively independent of the magnitude of the initial deformation. It will be seen from the data presented later that the definition does not accomplish this purpose very well.

A complication arises in the use of the definition in that it is necessary to select some arbitrary time interval as marking the end of the initial elongation and at which to measure l_s. To avoid uncertainty in determining this initial elongation, the ratio l_t/l_0 has been used by Wildschut[8] to designate creep. This has the disadvantage of not furnishing any basis for distinguishing between the ordinary elastic deformation and the subsequent slow deformation usually thought of as creep.

In this work it will be assumed that creep processes of flow start simultaneously with the ordinary elastic deformation, so the ordinary elastic deformation is to be deduced by extrapolation of a suitable long term creep curve to zero time. In the experiments to be described, this procedure applies a correction but does not change the results materially from those secured by using the period of extrapolation as the arbitrary start of the creep process.

The same notction as that shown in Figure 1 may be used, but l_s is now thought of as being the stretched length resulting from the ordinary elastic deformation alone, a correction having been made for any contribution caused by creep. l_0 is the initial unstretched length, and l_t the stretched length at any time t. The relative length, R.L., is here defined as the ratio l_t/l_s.

The ordinary elastic elongation, E_0, is given by:

$$E_0 = \frac{100(l_s - l_0)}{l_0} \tag{1}$$

It follows that:

$$\frac{l_t}{l_0} = R.L. \left(\frac{E_0}{100} + 1 \right) \tag{2}$$

The elongation, E_t, at any time, t, is given by:

$$E_t = R.L. (E_0 + 100) - 100 \tag{3}$$

The per cent creep, as previously defined, can now be expressed as:

$$\text{per cent creep} = 100 \frac{E_t - E_0}{E_0} = 100(R.L. - 1) \left(\frac{E_0 + 100}{E_0} \right) \tag{4}$$

During a creep test the rubber usually acquires a permanent set which becomes evident when the test is discontinued at time t. Let Δl_0 be the increment to l_0 due to permanent set. The contribution which Δl_0 made to the length, l_t, is, to a first approximation:

$$\Delta l_0 \left(\frac{E_0 + 100}{100} \right)$$

To secure the value of the primary, *i.e.*, reversible or recoverable, creep, the observed value should be corrected for the permanent set. This can be done by subtracting the above quantity from l_t in the definition of creep as given by

Equation (4).   When this is done, it follows that:

$$\text{primary creep} = \text{observed creep} - \left(\frac{E_0 + 100}{E_0} \right) \times \text{permanent set} \quad (5)$$

The values are in percentage.

An advantage of expressing the creep as percentage change in elongation is that it permits this simple subtractive correction for the permanent set.

A method which appears to permit the determination of the ordinary elastic elongation with an accuracy which is satisfactory for these experiments will now be described.   With the relative length plotted against the time, curves are secured such as those of Figure 2.   These can be extrapolated from the five minute point to zero time with reasonable precision, so that the length measured at five minutes after load application can be corrected to give the length corresponding to the ordinary elastic deformation.   Usually the correction is not very large.   For the curves shown in Figure 2, it is 1.5 per cent and 3.5 per cent, respectively, for the high and low elongation.
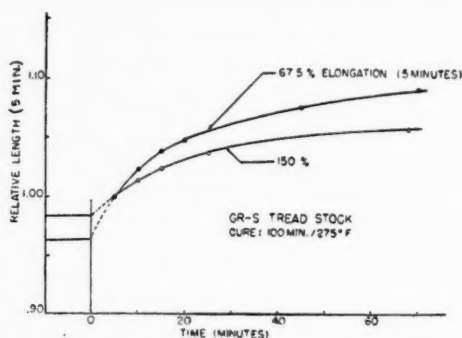
Fig. 2.—Curves illustrating extrapolation to zero time.

When the load is removed after the creep test, there is an initial rapid retraction followed by a slow retraction which is called recovery.   Recovery, like creep, is a flow process.   Analogously to creep, it may be defined as the percentage change in the initial deformation, the initial deformation being the rapid retraction when the load is removed.   Or, to avoid the ambiguity involved in determining the initial deformation, the ordinary elastic deformation for recovery can be determined in the same manner as previously described for creep, *i.e.*, by extrapolating the curve of relative length *vs.* time to zero time. According to these ideas:

$$\text{percentage recovery} = 100 \frac{l_{ru} - l_{rt}}{l_{r0} - l_{ru}} \quad (6)$$

where:

        l_{r0} is the stretched length before the load is removed
        l_{rt} is the length at time t
        l_{ru} is the length corresponding to the ordinary elastic retraction

For recovery, let the relative length be defined as:

$$R.L. = \frac{l_{rt}}{l_{ru}} \quad (7)$$

Then:

$$\text{percentage recovery} = 100\,\frac{(1 - R.L.)l_{ru}}{l_{r0} - 1} \qquad (8)$$

This definition may be readily understood when it is realized that it has the same form as for the case of the creep of a test-piece under compressive stress. The sequence of length changes which ensue on removal of the load are analogous to those which occur for a test-piece loaded in compression.

EQUATIONS FOR CREEP CURVES

The empirical description of creep curves for many different types of materials favors an equation in which the strain is essentially a linear function of the logarithm of the time in the earlier stages of the creep process. This has been suggested by both Braun[9] and Wildschut[8] for rubber.

Lyons[10] has advocated, as the most generally acceptable empirical law of creep, an equation of the form:

$$\epsilon = \epsilon_1 + at + b \log t \qquad (9)$$

ϵ is the strain at time t. ϵ_1, and a, and b are parameters, the values of which depend on the material and experimental conditions.

At the start of the creep process, the logarithmic term predominates. For longer times, the linear term becomes more important. The result of this is that when the strain is plotted against logarithmic time, the straight line obtained at the start trends to bend toward the strain axis as time goes on.

EXPERIMENTAL METHOD

The procedure for making the creep measurements consisted of hanging weights on $\frac{1}{8}$-inch wide, 2-mm. gauge, dumbbell test-pieces in a constant temperature cabinet with glass sides through which the samples could be observed
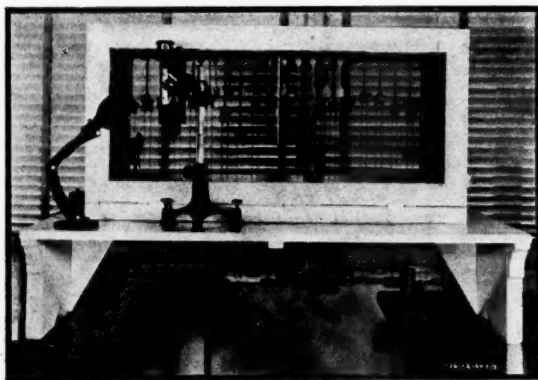
Fig. 3.—Photograph of creep test apparatus.

with a measuring microscope. The arrangements are apparent in Figure 3. The temperature was 35° C. It has been found advantageous to determine the gauged length as the distance between the ends of two lines ruled parallel to the length of the test-piece with a ruling pen and white, pigmented rubber

cement.   If the lines are ruled across the test-piece, they are broadened on stretching.   When ruled parallel to the length of the test-piece, the ends are sharpened on stretching and furnish very satisfactory points on which to set the cross hair of the measuring microscope.

The creep tests were made under constant load conditions, the stress increasing during the test because of reduction of cross-section as creep progressed. An experimental procedure has been used by Speakman[11] to avoid this effect. It would also be possible to make corrections for the change in area from a family of curves at different elongations, as suggested by Wildschut[8].   Since this involves the assumption that the structure is independent of the time-load relationship, it did not seem advisable to do this.

Constant stress conditions would make possible more exact comparison with present theories, but the results would have less practical significance.

Permanent set was determined 1000 hours after the load was removed, the test-pieces remaining in the thermostat at 35° C.   To determine the permanent set resulting from various durations of the creep test, it was, of course, necessary to use a different test-piece for each point of the curve.

COMPOUNDS

The formulas for the compounds used are given below:

GR-S	100		
Hevea		100	100
Sulfur	2.0	2.75	3.0
Zinc oxide	5.0	5.0	3.0
Mercaptobenzothiazole	1.5	1.35	1.0
Stearic acid	2.0	3.0	4.0
Softener	3.0	3.0	3.75
Phenyl-β-naphthylamine	1.0	2.0	1.0
E.P.C. black	50.0	50.0	

RESULTS

Figures 4 and 5 show plots of per cent creep *vs.* logarithmic time for a series of elongations for Hevea gum stock and Hevea and GR-S tread stocks.   The
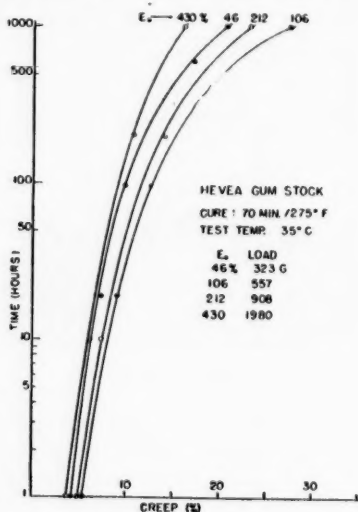
FIG. 4.—Effect of elongation on creep.
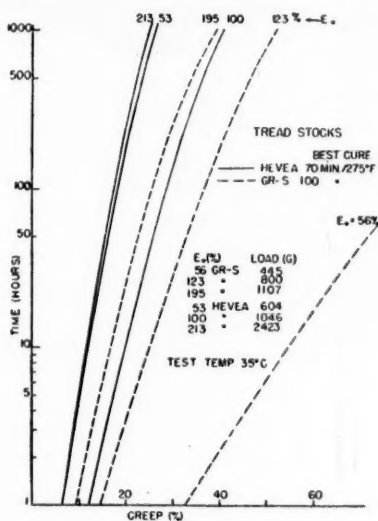
FIG. 5.—Effect of elongation on creep.

structural changes which occur because of crystallization make the creep phe-
nomena for Hevea complicated and difficult to interpret. It is noteworthy
that the Hevea stocks show the greatest creep rates for intermediate elongations
where the structure is partly amorphous and partly crystalline, a fact which has
already been recorded in the literature[12]. For GR-S, on the other hand, creep
diminishes monotonously for higher elongations. This contrast in the effect
of elongation on the creep for the two types of rubber correlates to some extent
with hysteresis and relaxation observations which show GR-S to improve
relative to Hevea in respect to both relaxation and hysteresis at higher elonga-
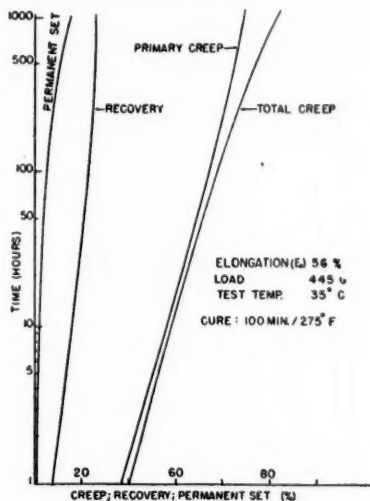
FIG. 6.—Creep, recovery, and permanent set for GR-S tread stock.
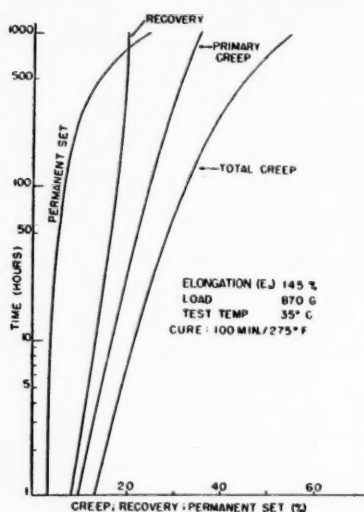
Fig. 7.—Creep, recovery, and permanent set for GR-S tread stock.

tions[13].   The mechanical instability of the molecular structure of GR-S at low elongations appears to be a fundamental weakness in comparison with Hevea.

All of the creep curves shown exhibit a characteristic concavity toward the strain axis when the ordinate is logarithmic time.   Figures 6, 7, and 8 illustrate creep curves before and after correcting for permanent set.   The correction improves the linearity of the creep curves.   Frequently, it results in a slight curvature in the opposite direction.   Considering the approximate nature of the correction, the assumption that the true primary creep curve would be essentially linear in this type of plot seems to be well justified.
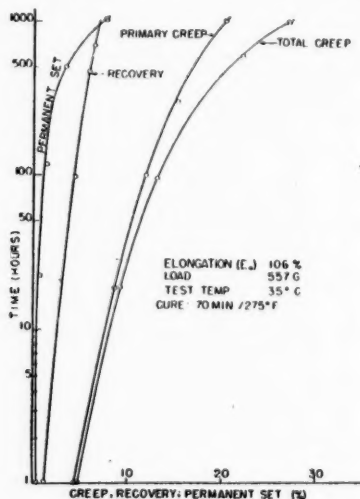
Fig. 8.—Creep, recovery, and permanent set for Hevea gum stock.

The general empirical equation for creep curves, Equation (9), accounts for the curvature on the semilog plot by means of a linear term representing a viscous type, constant-rate flow. Permanent set is not linear with time, as shown by the curves of Figure 9, although it becomes linear after a relatively
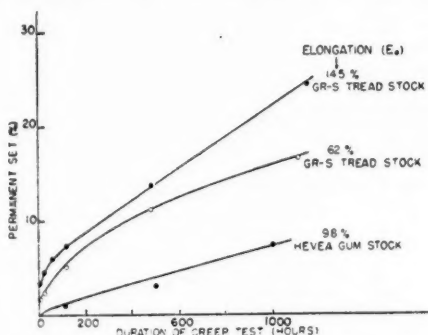
FIG. 9.—Dependence of permanent set on duration of creep test.

short time. Hence the contribution of permanent set to creep does not correspond exactly to this linear term, although correction for permanent set has the effect of making the creep very closely a logarithmic function of the time for the cases studied.

Figures 6, 7, and 8 also show recovery curves. The rate of recovery is considerably less than the rate of creep. The recovery curves show some curvature in the opposite direction from that of the creep curves, since a constant length must be approached asymptotically as time goes on, whereas in a creep test the length may increase indefinitely until rupture. Recovery is activated by the residual retractive tendencies of the network structure, a return to a
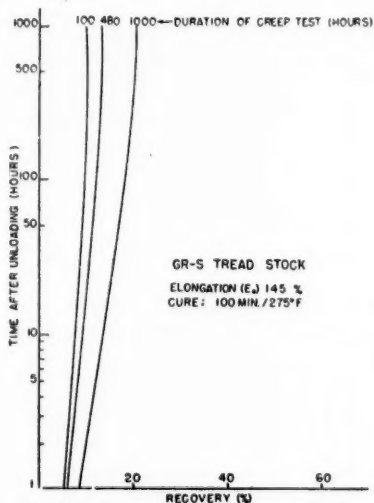
FIG. 10.—Recovery after creep test.
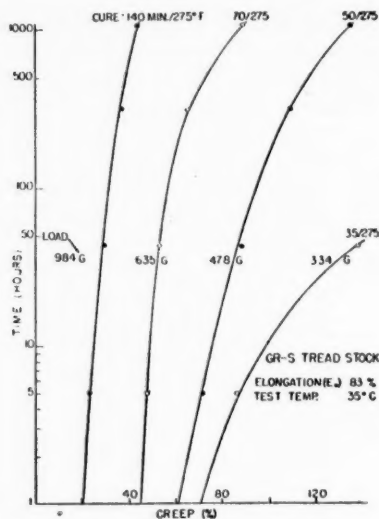
FIG. 11.—Effect of cure on creep.

condition of higher entropy. Theories of creep which require an extenal force to supply the activating stress do not apply directly.

Although, from Figures 6 and 7, the recovery curves for GR-S are rather insensitive to the elongation for the creep test, they show a systematic dependence on the duration of the creep test, as illustrated in Figure 10. As might be expected, the residual elastic forces in the network structure depend on the deformation which remains because of primary creep when the load is removed after the creep test. The magnitude of this deformation depends, in turn, on the duration of the creep test.
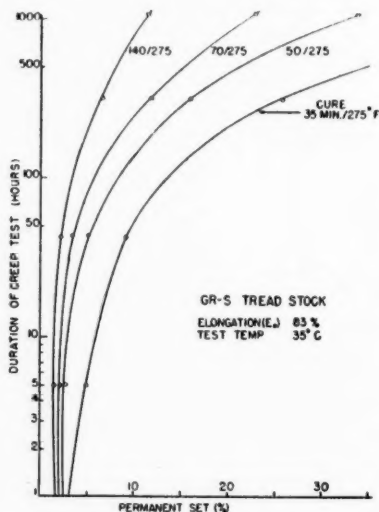
FIG. 12.—Effect of cure on permanent set.

The effect of cure on creep and permanent set for GR-S is shown by the curves in Figures 11 and 12.   The 35- and 50-minute cures are decidedly under optimum cure, and show large values for creep and permanent set.

Table I gives data on the relative proportion of permanent set and primary creep in dependence on cure.

TABLE I

CREEP AND PERMANENT SET FOR GR-S TREAD STOCK; $E_0 = 83\%$

Cure	A Permanent set (%)	B Creep (%) (1000 hrs.)	C Primary creep (%)	$\frac{C}{A}$ Primary creep permanent set
50/275	34	138	63	1.9
70/275	23	89	38	1.7
140/275	11	44	20	1.8

The strengthening of the primary-valence network structure by vulcanization could reduce flow by reducing the rate, the magnitude, or both the rate and magnitude of the molecular displacements.   It is reasonable to suppose that only the larger unit molecular flow processes result in permanent set.   Since
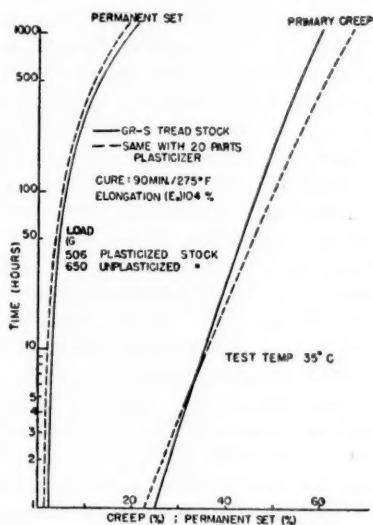
FIG. 13—Effect of plasticizer on creep.

the proportion of primary creep to permanent set is not affected appreciably by the extent of the vulcanization, it is most probable that vulcanization reduces the rate of the unit molecular flow processes and does not affect their size distribution or general character.   As vulcanization progresses, a larger part of the stress is carried by the relatively stable primary valence network, but the molecular units of flow which remain appear to function in essentially the same way.   For short term creep tests, up to about 48 hours, it was found that vulcanization did tend to reduce primary creep relative to permanent set, but the long term tests here reported seem to be of more general significance.

Figure 13 presents data secured for the GR-S tread stock with 20 parts of plasticizer (Paraflux) added. The possible lubrication of secondary valence bonds by the plasticizer has a surprisingly small effect on both the permanent set and the primary creep, although some enhancement of primary creep is definitely indicated. Any instability introduced into the molecular structure by the plasticizer was very nearly compensated for, as far as flow was concerned, by the lower stress applied to the plasticized stock in this test. It would be very desirable to extend the experiments to other temperatures to determine activation constants for the flow resulting in permanent set as compared to primary creep. This would be a means of securing additional information as to the molecular flow mechanisms responsible for the two types of flow.

For Hevea tread stock at high elongations all of the creep was accounted for by permanent set. What is known of the structure of Hevea at high elongations leads to the suggestion that, in this case, flow occurs in the amorphous material between the crystallites, with whole crystallites being displaced with reference to each other. Under such circumstances, the original relative molecular configurations cannot be reassumed upon removal of the stress.

SUMMARY

A study was made of creep, recovery, and permanent set of Hevea and GR-S over a 1000-hour period and a range of elongations at 35° C. Creep of GR-S is greater than that of Hevea. The stress of GR-S is considered to be supported to a greater extent by a relatively unstable secondary bond structure. This is consistent with the large creep values of GR-S at low elongations and the large ratio of primary or recoverable creep to permanent set. Hevea, in contrast, shows low creep at both high and low elongations and maximum creep at intermediate elongations for which the structure is heterogeneous, consisting of amorphous and crystalline phases.

A procedure was worked out for determining the contribution of permanent set to the observed creep. The creep curves were concave to the strain axis when plotted against logarithmic time. After correction was made for permanent set, they were found to be approximately linear, thus extending the range of application of the Tobolsky-Eyring theory of creep.

At the start of the creep test the flow appears to be due largely to the reversible yielding of relatively weak bonds which can reform under the action of the elastic network when the stress is removed. For longer periods of time, or for higher elongations, the flow involves more deep seated changes in structure. Larger units of structure are displaced or stronger bonds broken with resultant permanent molecular displacements upon removal of the stress. For Hevea at high elongations all of the flow was accounted for by permanent set.

ACKNOWLEDGMENT

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FACTORS INFLUENCING THE CONFIGURATION
OF CARBON PARTICLES IN RUBBER *

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Introduction.—The distribution of carbon-black particles in well mixed stocks of rubber takes more than one form. A perfect dispersion may be regarded as one in which every particle of colloidal carbon is insulated from every other particle by a film of rubber. This condition, though presumably theoretically possible, is never achieved in practice, and indeed it is by no means certain that if it could be achieved it would give optimum reinforcement to the system. At the other extreme is the condition where the carbon particles are all joined together in a three-dimensional network, and where full contact with the rubber molecules is confined to a small proportion of the particles. The latter condition is most nearly realized in electrically conducting rubber, where chains of carbon particles form conducting paths for the electric current. In the average rubber-black vulcanizate there is evidence, as will be seen, of both individual particles and chains of carbon. The relative abundance of the different modes of particle distribution depends in general on the nature of the black and the previous history of the stock. Changes in treatment before the vulcanization operation modify the mechanical and electrical properties of the vulcanizates possibly as a result of rearrangements of the carbon particles. There is disagreement on the actual nature of the changes which take place, and the work discussed in the present paper was designed to throw further light on the problem.

Historical.—It has long been assumed that particles of channel black tend to flocculate during the vulcanization process. Mention should be made of the studies by means of the optical microscope of Depew and Ruby[5], Green[8], Grenquist[7], Park and Morris[11] and Park and McClellan[10]. Grenquist concluded that, during curing, when the high temperature causes increased mobility of the rubber and fillers, there is a flocculation of previously dispersed particles. This flocculation, according to him, also takes place when a mixture of rubber and carbon black alone are heated.

There is a limited solubility of highly loaded channel black-rubber stocks in benzene and other solvents, and the fraction of rubber which dissolves does not in general carry any black with it from the stock. This phenomenon was attributed by Depew[4] to flocculation of the black, though Twiss[18] had previously suggested the alternative explanation of an adsorptive attachment of rubber and black. The work of Stamberger[16,17] and Blow[1], which showed that the properties of unvulcanized channel black-rubber stocks change on standing at room temperature, led them to conclusions substantially in agreement with those of Twiss and opposed to those of Depew.

The problem was carried a step further by Gerke, Ganzhorn, Howland and Smallwood[6], who described the effects of temperature in the range 140 to 190° C

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on channel black-rubber stocks either during or subsequent to the milling operation. These authors reported a stiffening of the stock and a considerable decrease in its electrical resistivity following the heat treatment. This they attributed to a severe flocculation of the carbon particles into chainlike networks. On remilling, the resistivity increases enormously, suggesting deflocculation, and does not decrease during vulcanization unlike its behavior in conventionally mixed stocks. Work[12] in the Dunlop laboratories confirmed most of the experimental data of Gerke *et al.* Among the changes in physical properties of vulcanizates produced from heat treated rubber-black stocks are a decrease in hysteresis (increase in resilience), a small decrease in tensile and tear strength, a reduction in hardness and a small increase in abrasion resistance.

In 1942 four British patents[2], taken out by the United States Rubber Company, claimed that the effects of the heating process can be greatly accelerated by the incorporation of certain organic chemical compounds in the rubber. These claims have been examined in the case of certain of the substances specified, and some of the test data are discussed in the following pages.

The electron microscope is now being employed not only to determine the particle sizes and shapes of the different types of carbon black, but also in the examination of sections of carbon-loaded rubber compounds. The publications of Wiegand and his coworkers should be particularly mentioned in this connection. Ladd and Wiegand[9] consider that "reticulate chain structure" is characteristic to a greater or less degree of most, if not all, forms of particulate carbon before it is milled into rubber and that it persists in certain cases after milling. Wiegand[19] had previously demonstrated a low persistence in the case of fine thermal black (*P*-33), in which structure is weakly developed and a high persistence, in the case of the strongly structure-forming Shawinigan acetylene black. Channel blacks, except those specially treated to promote high electrical conductivity in rubber, do not possess a high degree of reticulate structure, although Ladd and Wiegand[9] point out that in dry dispersions some of the particles show chain alignment. These authors show electron micrographs of vulcanized rubber in which the channel black appears to exhibit "a large number of discrete particles and short chains". They also show pictures of high modulus and semireënforcing furnace blacks in vulcanized rubber in which there are few discrete particles, but many chains of moderate length. Ladd and Wiegand conclude that, in vulcanized specimens, chain structure is not due to flocculation of individual carbon particles, but that such chains as are present are segments of chains originally of greater length.

Bulgin's researches[3] on electrically conductive rubber have led him to conclusions in some respects at variance with those of Ladd and Wiegand. He suggests that "carbon particles in rubber are at first distributed as individual particles by the shearing action of milling, but the individual particles are in a state of Brownian movement due to the kinetic energy of the system". The particles, which have a disordered crystalline structure and therefore possess relatively high free surface forces, cohere when they come into contact with each other. The structure thus formed can be broken by external forces, such as remilling, and can reform during the vulcanization process.

BENZIDINE AND HEAT TREATMENT

Among the organic compounds stated by the U. S. Rubber Company technologists[2] as accelerating the effects of heat treatment are urea, thiourea, and benzidine. Experiments were, therefore, made in which these three sub-

stances were incorporated into channel black-rubber stocks and subjected to heat treatment in a pan at a steam pressure of 70 lbs. per sq. in. (158° C). The following stocks were mixed:

	1	2	3	4
Pale crepe rubber	100	99	99	99
Channel black	45	45	45	45
Urea	—	1	—	—
Thiourea	—	—	1	—
Benzidine	—	—	—	1

Each stock was divided into three equal parts, one being left untreated, the second heated for 20 minutes and the third heated for 60 minutes. Finally, all the twelve stocks were mixed into a standard type of tread compound. Results of certain tests on the vulcanizates at optimum cure are given in Table 1.

All the compounds, after 60 minutes' heating of the unvulcanized stocks, increased in electrical resistance at least seventy-fold to a value beyond the range of the instrument available when these experiments were made. This effect was also achieved with the unheated benzidine compound and with the urea and thiourea compounds after only 20 minutes' heating. All three sub-

TABLE 1

Compound and treatment of unvulcanized stock	B.S.I. Hardness	Resilience (per cent rebound)
Control		
No heating	61	68.3
Heated 20 minutes	67	71.4
Heated 60 minutes	74	73.6
Urea		
No heating	54	70.6
Heated 20 minutes	59	75.4
Heated 60 minutes	62	77.5
Thiourea		
No heating	55	70.3
Heated 20 minutes	58	74.1
Heated 60 minutes	62	76.3
Benzidine		
No heating	63	76.6
Heated 20 minutes	68	79.0
Heated 60 minutes	72	80.0

stances have an influence in themselves on physical properties. This is partly due to their acting as mild secondary accelerators. (Activators of acceleration usually increase both resilience and hardness), and in the case of urea and thiourea most of the increase in resilience not accounted for by heat treatment might possibly be explained in this way. With benzidine, however, such an explanation is insufficient to account for most of the increased resilience of the vulcanizates made from stocks which had not been heat treated, and some effect on the carbon-rubber system is strongly suggested. The results indicate that the effects of heat treatment and benzidine are additive.

To determine the manner in which benzidine influences black-rubber stocks, a number of experiments of various kinds were carried out. One result of this further work was to confirm the conclusions of Zimmermann and Cooper[20]

that benzidine acts as a stiffener or antisoftener of unvulcanized rubber. Partly for this reason and partly because of its accelerating effect on curing, benzidine seriously increases the scorching rate of uncured stocks. The properties of the vulcanizates depend partly on the milling and mixing treatment. To get the full effect of the benzidine on resistivity, resilience and hardness, it is desirable to prepare a stock of rubber, black and benzidine, and to complete the mixing on the following day. The data of Table 2 illustrate this point.

TABLE 2

	Tread compound, mixed in one operation		Tread compound, mixed in one operation with 0.5% benzidine		Tread compound, using masterbatch containing rubber 100, black 50, benzidine 0.5%	
	Unaged	Aged 20 days at 80° C	Unaged	Aged 20 days at 80° C	Unaged	Aged 20 days at 80° C
Tensile strength (lbs. per sq. in.)	3,280	2,320	3,290	1,880	3,170	1,580
Per cent elongation (700 lb. per sq. in.)	220	160	225	155	220	160
B.S. hardness	64		74		88	
Resilience (per cent rebound)	67		71		76	
Resistivity (ohm-cm.)	4×10^8		5×10^9		10^{14}	
Relative abrasion resistance	100		96		98	

It has been found that tear resistance, judged by the block-tearing test, although not always influenced by benzidine alone, is invariably decreased by the combined action of benzidine and heat treatment. Table 3 illustrates the poor tearing properties of a tread vulcanizate after heat treatment of the rubber-black masterbatch in which benzidine had been incorporated. Hardness and resilience values show the usual trend, and tensile strength is slightly reduced.

TABLE 3

	(a) Compound with benzidine (one operation)	(b) Compound using masterbatch of rubber 100, channel black 50, benzidine 0.5%	(c) As (b) but heated 45 minutes at 70 lbs. per sq. in. steam
Tensile strength (lbs. per sq. in.)	3,230	3,100	2,960
Per cent elongation at 700 lb. per sq. in.	190	185	195
B.S. hardness	57	64	83
Resilience (per cent rebound)	66.2	70.6	73.1
Tear strength (lbs. per half in.),			
20° C	141	146	97
100° C	126	126	85

The effect of heat treatment and benzidine on GR-S-channel black compounds is in general similar to that on natural rubber. Figure 1 illustrates the changes in resilience and tear resistance of vulcanizates produced from channel-black stocks of rubber and GR-S (polymer 100, black 45) with and without 0.5 per cent benzidine, heated and unheated. In this experiment both standard channel (MPC) and conductive channel (particle size similar to that of MPC) were employed. Conductive channel black stocks do not respond to heat
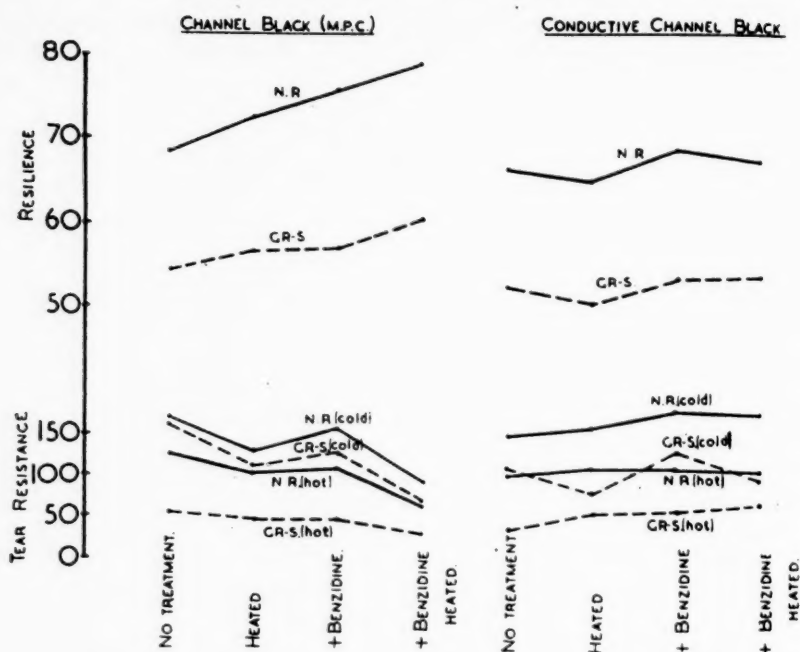
Fig. 1.—Effect of heat treatment and benzidine on resilience and tear resistance.

treatment in the usual way, there being little change in resilience and specific resistance. The values of B.S. hardness and electrical resistance of the natural rubber vulcanizates are given in Table 4.

TABLE 4

Type of black and treatment of rubber-black stock	B.S. hardness of vulcanizate	Specific resistance of vulcanizate (ohm-cm.)
MPC Black		
No treatment	64	2.1×10^6
Heated	84	$>2.4 \times 10^{10}$
Plus benzidine	70	$>2.4 \times 10^{10}$
Heated plus benzidine	82	$>2.4 \times 10^{10}$
Conductive Channel Black		
No treatment	62	111
Heated	66	108
Plus benzidine	57	166
Heated plus benzidine	61	225

ELECTRICAL RESISTANCE CHANGES

Effects of temperature, time and strain.—It was found that the addition of benzidine to channel black-rubber stocks does not have the effect of decreasing the resistivity of the unvulcanized stock, as does heat treatment, but that it actually increases it upwards of a hundred-fold. This suggested that, whatever is the action of benzidine on the carbon, it is not that of an activator of flocculation. The evidence thus far seemed contradictory, since it appeared to be a

reasonable hypothesis that the properties of vulcanized heat-treated stocks were related to an initial flocculation resulting from heating[6,12] and that benzidine speeded up the process. The view had been provisionally accepted that there is a slow flocculation of carbon particles at room temperature in unvulcanized rubber and that heating accelerated the flocculation by increasing the thermal energy of the system and decreasing its viscosity. It was therefore decided to investigate in detail the resistivity changes taking place in unvulcanized channel black stocks under different conditions, since it was assumed that such changes in electrical resistance would indicate changes in the structural arrangement of the carbon particles brought about on the one hand by flocculation of individual particles and on the other by deflocculation of existing chains.

Resistance measurements were made on stocks immediately after mixing and at rapid intervals on standing. The mixings were made on a 12-in. laboratory mill and consisted by weight of (a) rubber 100, channel black 40, stearic acid 3, and (b) rubber 100, black 50, stearic acid 3 and benzidine 0.5. The
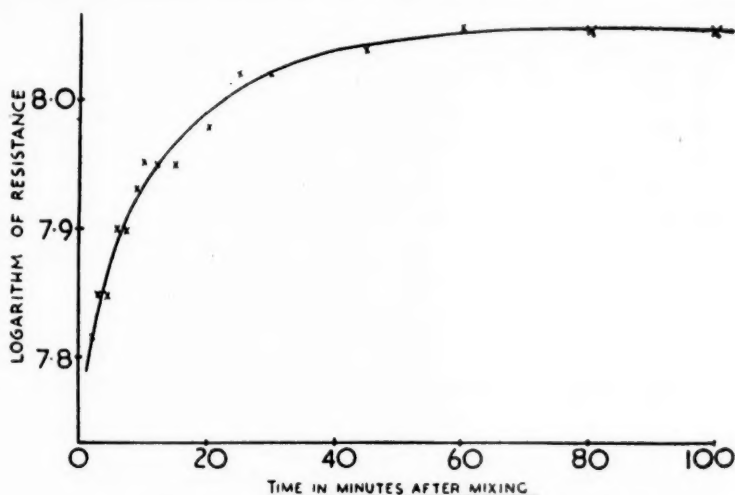
Fig. 2.—Changes in the resistance of a 100-rubber, 40-channel black stock during cooling and standing after mixing.

mixing temperature of both stocks was about 65° C. One of the log resistance-time curves is shown in Figure 2. In both cases the resistance rises rapidly at first as the sample cools and then tends to reach a steady value. This change appears to be explained by temperature changes. Bulgin[3] had shown that vulcanized conductive rubber has in general a negative value of temperature coefficient of resistance. It was found in the experiments now under consideration that, once the specimens had reached a steady temperature, the resistances remained substantially constant for several days provided the specimens were not strained. This experiment seems to show that channel black does not flocculate into chains on standing after mixing; if it did a decrease of resistance with time ought to take place. It should be added that precautions were taken to keep the condition of the samples as constant as possible, since Bulgin's

work on vulcanized conducting rubber had demonstrated that flexing may increase the resistance at a given temperature.

It was found that momentary stretching or flexing of unvulcanized rubber-channel black stocks could, in fact, increase their electrical resistance appreciably. Figure 3 shows the effect of differing degrees of stretch on the resistance at room temperature of a sample which had been previously heated to a high temperature (150° C) such as might be expected to promote preliminary flocculation of the black. The measurements were made 20 minutes after stretching, so the resistance had reached an approximately steady value. Quite a small percentage elongation is sufficient considerably to increase the resistance under the conditions of this experiment.

It seems reasonable to make the tentative assumption at this stage of the enquiry that resistance changes accompanying changes in the temperature of unvulcanized rubber can be divided into two parts: (1) those inherent in the
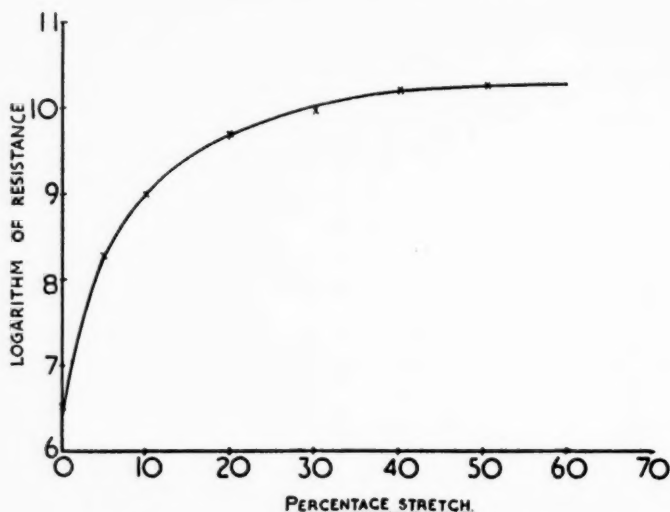
FIG. 3.—Effect of stretching on the resistance at 20° C of a 100-rubber, 50-channel black stock after heating to 150° C and cooling.

carbon particle complex itself, the resistivity of which changes according to the value of the temperature coefficient of resistance of the carbon and of any gaps between particles which may be conductive owing to electron jumps, and (2) those caused by changes in the structural arrangement of the carbon particles, *i.e.*, changes to denote which the terms "flocculation" and "deflocculation" have been rather loosely employed. The authors propose to substitute the more precise terms *catenation*, which implies the formation of chain structure, and *decatenation*, the breaking down of such structure. Resistance changes in the carbon particle complex itself are reversible within the temperature range considered; those dependent on the degree of chain structure may or may not be reversible.

Changes in resistance of rubber-channel black stocks with temperature were determined on 1-mm. calendered sheets, which quickly attained the temperature of the oven and could be conveniently stretched. The electrical

resistance of an unvulcanized channel-black stock decreases with temperature, and it was found that in the case of a sample momentarily strained at room temperature and then heated to, say, 100° C, there is initially a very rapid decrease of resistance with time. If the temperature is then kept constant the resistance remains constant. Figure 4 illustrates the changes in resistance of a 100 rubber-40 channel-black stock after being momentarily stretched 25 per cent at three temperatures, the temperature being maintained constant for prolonged periods during each experiment. The curves show that the speed of recovery to a steady value increases with temperature, and at 100° C recovery is practically complete within two minutes. After 16 hours at this temperature the resistance was practically unchanged.

Further experiments showed that Bulgin's recovery of different rates of change of resistance with temperature, according to whether samples are flexed or not flexed, applies to unvulcanized mixtures of rubber and nonconducting reinforcing blacks, as well as to vulcanized conductive channel-black
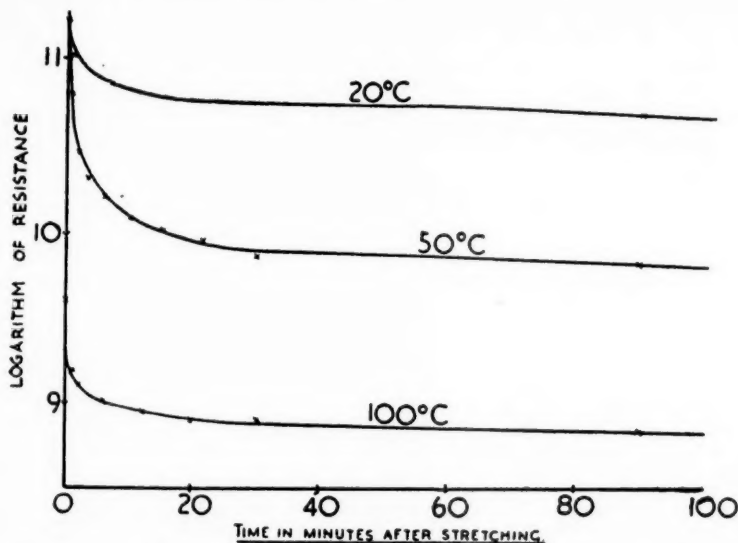
FIG. 4.—Effect of stretching, temperature and time on a 100-rubber, 40-channel black stock.

mixes. The curves of Figure 5 which illustrate the changes that take place in vulcanized stocks, are generally similar to those figured and discussed by Bulgin for vulcanized rubber. The drop in resistance of a 100 rubber-50 channel-black stock follows the line A.B.C. as the temperature is increased after momentary stretching (25 per cent) at 20° C. On cooling from 100° C, the resistance follows the line B.D., or from 160° C, the line C.E. These are metastable values, since stretching at 20° C or at any temperature below the highest reached results in an immediate increase in resistance to a value usually higher than that which it had at the same temperature on the ascending curve A.B.C., but which soon falls again to the latter value, which is the stable one. It appears that any catenation due to heating is reversible on cooling and straining. Table 5 shows that the resistance after a momentary stretching
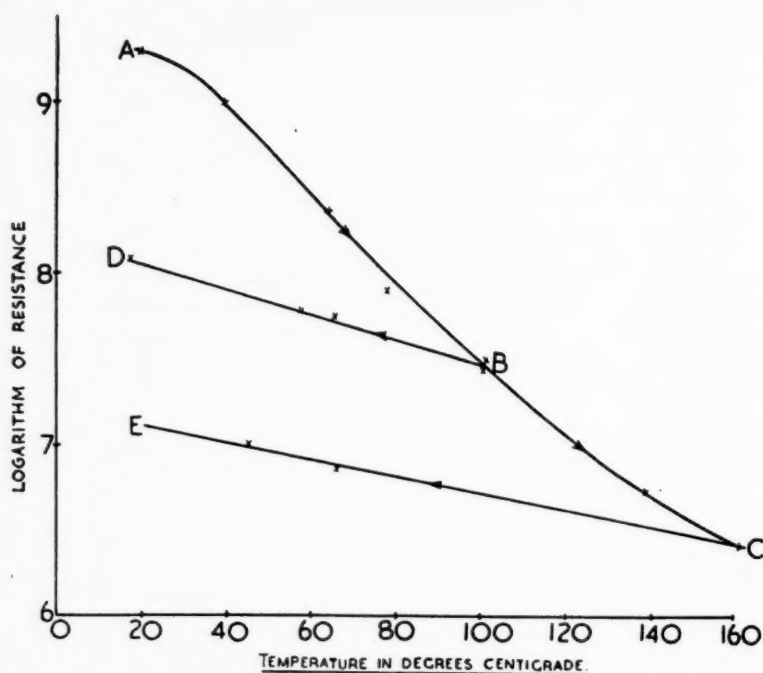
FIG. 5.—Effect of heating and cooling after prestretching of a 100-rubber, 50-channel black stock.

of the rubber at room temperature is unaffected by a previous heating of the stock. (Where resistances after momentary stretching or flexing are given in this paper, the measurements were made not less than 15 minutes after straining the samples. The reason for this procedure will be understood by reference to Figure 4.)

These experiments throw doubt on the theory that channel black forms permanent or subpermanent chain structures following the initial mixing process, and so far as it goes is consistent with Ladd and Wiegand's conclusion[9] that any structure which is present results from a breakdown of chains originally of greater length. To throw more light on the problem, the effects of different mixing temperatures were studied, since it was argued that high-temperature mixing, by providing conditions of low viscosity and high thermal energy, might to some extent offset the effects of the shearing action which tends to break down the structure. Results are given in Table 6.

TABLE 5

| | Specific resistance | |
Condition before stretching	Before stretching	After momentary 25 per cent stretch
Unheated	—	6×10^9 ohm-cm.
Heated to 50° C and cooled	1.2×10^9 ohm-cm.	8×10^9 ohm-cm.
Heated to 100° C and cooled	1.2×10^8 ohm-cm.	7×10^9 ohm-cm.
Heated to 150° C and cooled	3×10^7 ohm-cm.	7×10^9 ohm-cm.

TABLE 6

SPECIFIC RESISTANCE OF RUBBER-BLACK STOCKS

Milling temperature (° C)	From mill unflexed	15 seconds after flexing	15 minutes after flexing	Heated to 100° C and cooled
45	9×10^{11}	2×10^{12}	9×10^{11}	9×10^{11}
66	10^8	8×10^9	8×10^8	10^8
120	10^7	2×10^8	10^8	2×10^7

The successively lower resistivities with increasing temperature of mixing are in line with expectations, and seem to indicate a less severe decatenation with increasing temperature. But it is necessary to consider the alternative possibility that a chain structure is built up during mixing. If the carbon, when it enters the rubber, consists of both chains and individual particles, it would appear possible that the latter, because of the mixing action, might be brought into sufficiently close proximity to enable them to cohere, and that the decreased viscosity and increased thermal energy of the rubber molecules accompanying a higher temperature might accelerate the process by increasing the Brownian motion or whatever mechanism is responsible for promoting catenation. On this view the degree of structure following mixing depends on a balance between one set of forces promoting catenation of individual particles and another set of forces causing decatenation of existing structures. It is to be noted that subsequent heating of the stocks to a temperature higher than that of mixing (Table 6), followed by cooling, does not result in a decrease in resistance, and this seems to show that the effect on reticulate structure of mixing at a moderate temperature followed by heating to a higher temperature is not the same as that of mixing at the higher temperature, and is an argument in favor of the view that the action of mixing on structure is purely destructive. Further support of this view was provided by remilling a stock at 100° C, which had originally been mixing at 65° C. The effect of remilling increased the resistivity from 5×10^7 to 7×10^8 ohm-cm.

There is no evidence from these experiments either that any catenation takes place during mixing or that if catenation occurs during subsequent heating in air it forms permanent structures. This raises the question of the validity of previous conclusions[2,6,12,15] that heating in the absence of air, e.g., in steam, the heat treatment described in this and earlier papers, promotes a strong catenation of carbon particles. A mixing of rubber 100, channel black 50, was therefore made at a temperature of 65° C, and subjected to a sequence of changes as indicated in Table 7, which records the specific resistance after the different treatments.

TABLE 7

Treatment	Specific resistance (ohm-cm.)
Before flexing	5×10^7
After flexing	3.6×10^8
Heated in steam at 70 lbs. per sq. in. and cooled	2.3×10^7
Reflexed	3.7×10^8

In this as in nearly all the experiments the specimens, which were $\frac{1}{4}$ inch thick, were allowed to contract during cooling, French chalk being used to lubricate the supporting surface. The result of not lubricating the samples during cooling is in effect one of straining. Two samples from the mix under consideration which were not allowed to contract during cooling gave resistivi-

TABLE 8

Changes in Specific Resistance During Remilling, Mixing and Curing

Treatment of sample	Using plain stock (rubber and black)				Using benzidine stock (rubber, black and benzidine)				Using plain stock, heat-treated			
	Stock	Portion of stock remilled	Mix completed	Vulcanized	Stock	Portion of stock remilled	Mix completed	Vulcanized	Stock	Portion of stock remilled	Mix completed	Vulcanized
Unflexed	4×10^7	2×10^8	2×10^9	—	9×10^8	5×10^{10}	4×10^{12}	—	4×10^7	3×10^{12}	4×10^{13}	—
Flexed	2×10^8	9×10^8	9×10^9	2×10^8	4×10^9	1.4×10^{10}	1.2×10^{12}	1.5×10^{11}	2×10^8	2×10^{12}	7×10^{13}	2×10^{13}
Heated to 140° C and cooled	4×10^7	8×10^7	2×10^8	1.2×10^8	1.5×10^9	6×10^{10}	2×10^{11}	5×10^{10}	4×10^7	2×10^{11}	1.3×10^{12}	1.6×10^{13}
Reflexed	7×10^8	4×10^9	8×10^8	5×10^8	2×10^{10}	2×10^{11}	5×10^{11}	5×10^{10}	7×10^8	3×10^{11}	13×10^{12}	6×10^{11}

CHANGES IN SPECIFIC RESISTANCE DURING REMILLING, MIXING AND CURING

ties of 1.3×10^8 and 1.2×10^8, respectively, which are significantly higher than those of the unflexed samples.   The latter, however, are not completely without strain, since they have been distorted during the mixing operation.   For this reason and owing to the fact that the samples reached higher temperatures during heating than mixing, the unflexed values after heating are lower than before heating.   The flexed values, on the other hand, are not significantly altered by the heat treatment.

On this evidence, the conductive properties of the mix before remilling are potentially unchanged by heat treatment.   This conclusion, which is supported by other data (Table 8), is at variance with the data of Gerke et al.[6] and it can only be suggested that their measurements did not take account of variable conditions of strain in the samples.   It is, in fact, extremely difficult to ensure uniform conditions of testing.
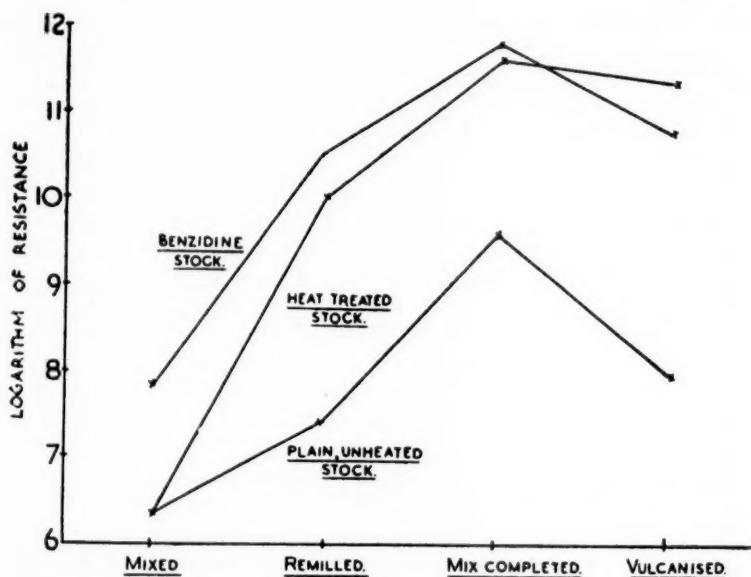
FIG. 6.—Effect of milling, mixing and vulcanizing on resistivity.

Effects of milling, mixing and vulcanizing.—Resistance measurements on unflexed samples at room temperatures were made at stages in the process from mixing to vulcanizing of the compound.   This was done with and without heat treatment of the rubber-black stocks and with and without benzidine. The stocks (rubber 100, channel black 50) were remilled before the mix was completed to observe the effect on the resistance of milling without adding more ingredients.   The heat treatment was carried out for 45 minutes in a steam pan at 70 lbs. per sq. in. steam pressure (158° C), and the benzidine was mixed into the black stock, which was then permitted to mature for a day before remilling and completing the mix.   The results are shown diagrammatically in Figure 6.

The chart shows that benzidine and heat-treated stocks undergo similar changes during remilling.   The following points are established.

(1) Benzidine helps milling to increase electrical resistance, particularly if it has been in the stock for several hours.
(2) After remilling the resistances of the benzidine and heat-treated stocks are both extremely high.
(3) In all cases completing the mix increases the resistance to a value appreciably higher than that reached after the previous remilling.
(4) During vulcanization the resistance of the completed mix is generally decreased, but it is not reduced to less than the value for the remilled stock.

It seems that remilling tends permanently to increase the electrical resistance of the stocks, so the inference appears to be that milling permanently decatenates channel black and that benzidine and heat treatment help in the process.
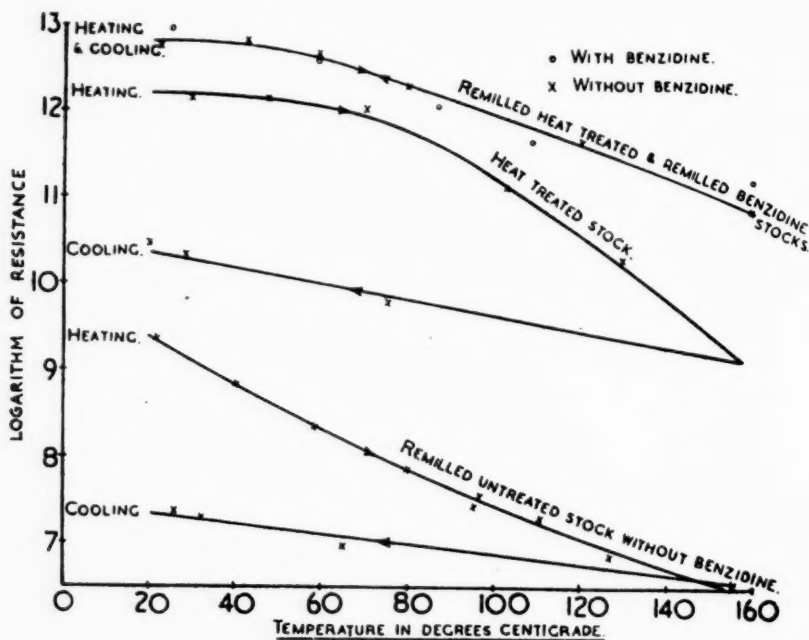
FIG. 7.—Effect of benzidine and heat treatment on resistance temperature changes after stretching.

In a later series of experiments resistance-temperature changes were determined on calendered channel-black stocks as follows: (1) untreated; (2) heated 45 minutes in steam at 70 lbs. per sq. in.; (3) heated and remilled; (4) untreated but containing benzidine; (5) with benzidine after remilling. Temperature-resistance curves are drawn in Figure 7 and show (1) the hysteresis effect due to stretching disappears in remilled heat-treated and remilled benzidine stocks, (2) it persists in heat-treated stocks before remilling and in remilled unheated stocks if benzidine is not present. Before remilling benzidine stocks show considerably less hysteresis than those without benzidine. The high initial resistance of the heat-treated stocks in these experiments is presumably due to calendering after treatment.

The reduced resistance after vulcanization may appear to conflict with the conclusion that heating has no permanent effect on the resistance. It was suspected that this phenomenon could be explained as a partial or complete recovery of the conductivity which had been lost during completion of the mix. A further experiment was made to include measurements of both the flexed and unflexed resistances and a direct comparison of the resistances of the completed mix and the remilled rubber-black stock. Unheated and heated stocks were divided into two equal parts, the one for completing the mix, and the other for remilling the rubber-black stock for the same time and at the same temperature as for mix completion. The results of this experiment are shown in Table 8. An examination was also made of the changes in resistance of the completed mixes during heating by states until they were vulcanized. The temperature reached was 140° C.

These experiments have shown that:

(1) Mix completion, using stocks containing only rubber and black, and possibly benzidine, results in a bigger increase in resistance than does remilling the stocks for the same time and at the same temperature.

(2) Most of this extra increase is temporary. Heating to temperatures in the region of 100° C, that is, before vulcanization takes place, is sufficient permanently to destroy most of the difference between stocks remilled with and without adding further ingredients.

The question arises, can the extra increase in resistance during completion of the mix be attributed to some ingredient assisting milling to decatenate the black? This does not appear to be the explanation, because changes due to milling have been found irreversible by heating. Further work will be necessary to determine which ingredient is responsible for the changes, and why.

SOLUTION EXPERIMENTS

The behavior of channel black-rubber mixes in solvents such as benzene and petroleum naphtha has been discussed by various authors[1,4,16,17,18]. Below a loading which varies according to the degree of mastication of the rubber, the mixing conditions, the quantity and nature of the softeners present and the duration of the period between mixing and solvation, some of the carbon in the mix diffuses with the rubber into the solvent, but above that loading the rubber which is extracted from the swollen stock contains no carbon. Migration of black takes place (if at all) most readily when the mix is solvated immediately after mixing, and it may be completely inhibited if the mix is allowed to stand for a sufficiently long period before it is placed in the solvent. Both adsorption of rubber on black[1,16,17,18] and flocculation of black[4] have been invoked to explain these phenomena.

It has been found that both heat treatment, as understood in this paper, and benzidine (together with certain other amines) act as powerful inhibitors of carbon migration into the solvent. The supposed facts with regard to heat treatment had seemed to favor the flocculation hypothesis, since this process was apparently accompanied by a decrease in electrical resistance. However, it has been shown on earlier pages that there is no evidence of permanent flocculation (or catenation) at either ordinary or elevated temperatures, and it has also been shown that benzidine does not promote catenation.

The effect on electrical resistance of mixing rubber-channel black stocks at three different temperatures has been described above. Portions of these

stocks were put into petroleum naphtha immediately after mixing and also after standing for 24 hours. It was found that the behavior of the black varied according to the milling temperature. In the case of the lowest temperature (45° C) much of the black went with the rubber into solution (a similar cold mixed stock using rubber considerably overmasticated broke down completely into a uniform solution); much less black diffused out of the stock mixed at 60° C, and none at all from that mixed at 120° C. In the case of the stocks which had been allowed to stand no black migrated from the stocks mixed at 66° and 120° C, while a reduced quantity came out of the stock mixed at 45° C. On the assumption that chain structure is more highly developed in stocks mixed at higher temperatures, these facts are consistent with the view that such structure is a factor in preventing migration of black into the solvent. It is obviously not the only factor, since migration of black is also retarded when the stock is allowed to stand before it is dissolved under conditions where no catenation occurs, and also when benzidine, which apparently helps de-catenation, is present.

Solution experiments following the remilling of heat-treated benzidine and nonbenzidine rubber 100, channel black 50, stocks have shown no migration of black, and in this respect the black behaves as it did before the stocks were heated.

A further point should be noted. The cold-milled stocks were rough, suggesting inadequate mixing and poor distribution of carbon. Some of the migrated black, therefore, may not have been wetted by the rubber. It is difficult to incorporate channel black in rubber at temperatures below the region of 50° C. Also the effective loading of the cold-milled stocks would be lower than that of the others with a consequent greater probability of black migration. (Channel black always migrates into the solvent when the loading is sufficiently low.)

The conclusion is that solution experiments provide no reliable evidence either of catenation or decatenation of channel black. They are consistent with the view that both carbon to rubber and carbon to carbon attachments exist in unvulcanized rubber.

CARBON BLACKS OTHER THAN CHANNEL BLACK

Mixtures of relatively coarse blacks such as semireinforcing furnace do not respond to heat treatment as do rubber-channel black mixtures, the physical properties of the vulcanizates being comparatively unaffected. Recently new types of furnace carbon almost as fine in particle size as easy processing channel have been produced, and it is of interest to determine the extent to which they are influenced by the heat treatment. Table 9 records comparative data on vulcanizates obtained from medium-processing channel (Micronex) and a

TABLE 9

Type of black and treatment	B.S. hardness	Resilience (per cent rebound)	Tear resistance (lbs. per half in.)	
			20° C	100° C
Micronex—unheated	70	64.9	143	91
heated 45 min.	85	71.2	105	74
Statex-K—unheated	80	73.1	106	71
heated 45 min.	83	75.4	100	79
heated 90 min.	82	76.6	84	54

reinforcing furnace black (Statex-K). The stocks submitted to heat treatment at a steam pressure of 70 lbs. per sq. in. consisted of pale crepe 100, black 50.

It should be noted in regard to the results of Table 9 that, whereas rebound and hardness are recorded to the optimum cure, tearing was only carried out at one cure, which was about optimum in the case of Micronex, but substantially beyond the optimum for the Statex-K stocks. The Statex values, therefore, should be compared only among themselves, and not with those of Micronex with which they would have compared better at an equivalent state of vulcanization. The data show that the effect on hardness and resilience of heating the reinforcing furnace-black stocks is less than that of the channel-black stocks. Tear resistance as usual seems to suffer by heat treatment, the decrease being similarly marked for each stock. Electrical resistance measurements were not made on these vulcanizates, but a later comparison showed that heat treatment increased the value of a Statex-K mix from 4.4×10^4 to 7.3×10^7 ohm cm.

The effect of heat treatment is still less marked on high-modulus furnace-black stocks than on reinforcing furnace stocks. The former type has coarser particles than the latter and possibly possesses more structure. Philblack

TABLE 10

Type of black and treatment	B.S. hardness	Resilience (per cent rebound)	Resistivity (ohm-cm.)
HMF (Statex-93)—unheated	67	81.7	9.6×10^6
heated	66	84.2	2.5×10^{13}
Philblack—unheated	56	80.8	2.1×10^4
heated	57	81.2	1.5×10^6
Shawinigan—unheated	52	79.0	1.2×10^3
heated	53	79.3	5.2×10^3
Conductive channel—unheated	49	61.3	8.6×10^2
heated	53	64.4	1.2×10^4

of similar particle size to HMF, but exhibiting a greater degree of reticulate structure, shows practically no response to heat treatment, and the same can be said of Shawinigan acetylene black, which has rather smaller particles than HMF, but shows still more structure than Philblack. These types are compared, together with a conductive channel black, in Table 10. The heat-treated stocks had the composition pale crepe 100, black 50 and the heating conditions were 45 minutes at 70 lbs. per sq. in. steam pressure.

Table 10 shows a small increase in resilience of the high-modulus furnace-black mix and a small decrease in hardness of the conductive channel mix following heat treatment; otherwise there is little effect on these properties. In all cases, however, resistivity has increased as in channel-black stocks, the increase being smallest in the case of Shawinigan black. The conductive channel-black of this experiment was of different origin from that of an earlier experiment (Table 4), which did not increase in resistance after heat treatment.

DISCUSSION

This investigation has shown that resistivity changes which take place in unvulcanized rubber on heating and cooling are completely reversible. The conclusion is reached that heat does not promote a permanent change in the arrangement of the carbon particles. On the other hand, changes in resistance resulting from milling the stock, without adding further ingredients, are not

reversible. Except in the case of certain conductive black stocks, remilling increases the resistance, presumably as a result of decatenation. In high-modulus furnace, reinforcing furnace and channel-black stocks, breakdown of the chains on remilling is particularly marked. A second remilling of the stock, with or without the addition of the remaining ingredients, including sulfur, further increases the resistance.

Recent work with the electron microscope in the Dunlop laboratories has confirmed the observations of Ladd and Wiegand[9] that reticulate structure is present in all types of particulate carbon before it is milled into rubber, and the question arises as to whether milling merely breaks down the chains into shorter lengths or in addition separates them completely into discrete particles. Both individual particles and short chains have been recognized by Ladd and Wiegand, and although many of the former may have entered the mix as individuals, some may have arisen as a result of decatenation. Opposing the shearing action of milling which breaks down the structure is a possible tendency, discussed above, to rebuild it because of encounters between carbon particles in the rubber due either to the mixing action or to Brownian motion or to both of these effects. If there is such a tendency it is masked by the shearing effect, particularly if the milling takes place at relatively low temperatures.

To account for the resistance changes taking place on heating and cooling after mixing, it was assumed at an early stage in the present study that some chain structure is developed during the period of heating. It is now necessary to look more closely into this assumption. Brownian movement has been invoked to explain any mobility which carbon particles might experience in rubber[3]. The following reasons throw considerable doubt on the view that Brownian motion of carbon particles does occur in rubber.

(1) At mixing temperatures immediately after milling, when the effect of shear, which tends to break down existing structures, is removed, individual particles might be expected to coalesce if they are in Brownian motion. Resistance measurements, however, show no evidence of catenation under these conditions.

(2) Remilling at a higher temperature than the first milling results in a higher resistance, suggesting decatenation. Under the conditions of decreased viscosity and increased thermal energy which would enhance Brownian movement some rebuilding of structure might have been anticipated.

(3) On the hypothesis of Brownian motion, individual particles have greater mobility than have groups or chains. If discrete particles catenate by Brownian movement during heating, they are unlikely to decatenate into their original configuration when the rubber is cooled and strained. To do this they would be expected to form chains which would break in every link when any strain was set up in the rubber; this seems unlikely. The fact that the resistance changes are completely reversible suggests that the particles do in fact assume their original configuration following heating, cooling and straining. It might be added that the condition for the chains to break in every link would appear to be such that each particle was firmly attached to the rubber, in which case recatenation by migration of the carbon particles would be impossible, and the original particle configuration would tend to be recovered when the strain was removed.

(4) Remilled heat-treated and benzidine stocks show no evidence of catenation on later heating, the resistivity depending on the temperature only. On

the Brownian motion hypothesis such a condition would only be expected in the absence of discrete particles, *i.e.*, where all the particles were linked together in sufficiently large groups or chains for Brownian movement to be inoperative. As a matter of fact electron micrographs of heat-treated vulcanizates show large numbers of individual particles, as is to be expected from their high resistivity. There seems no reason, judging from resistance measurements, to think that vulcanization brings about an appreciable change in the number of discrete particles. Admittedly on the hypothesis which is later put forward, we would expect benzidine and heat treatment to reduce the number of mobile particles by attaching more of the black to the rubber, but even if it is assumed that mobility of the black in treated stocks is prevented in this way, the hypothesis of Brownian movement cannot be accepted because evidence of temporary catenation is obtained in heat-treated stocks before they are remilled.

The above argument suggests that carbon particles are unlikely to migrate to any appreciable extent in unvulcanized rubber. If this be admitted, it becomes necessary to seek a different explanation for the apparent increase in chain structure which accompanies the heating of rubber-black stocks. Are there, in fact, any real changes in structure accompanying temperature changes? Can the resistance changes be accounted for in any other way? The sudden increase in electrical resistance when heated and cooled rubber is stretched or flexed results, we have assumed, from breaks in the structure which are healed when the rubber is reheated. If the particles themselves are immobile, what is the mechanism by which such structures are remade after being broken? The answers to these questions await the result of further research, but it is suggested that an explanation might be found from considerations of interactions between structures of carbon particles and reversible changes in the rubber which accompany heating, cooling and straining. There is the further possibility that an activation energy of bonds between the carbon particles may be involved in the explanation.

The data which have been presented in this paper indicate that the addition of benzidine to channel black stocks produces modifications of both unvulcanized and vulcanized compounds, which are in general similar to those promoted by heat treatment, and the presumption is that the mechanism is similar. The differences in physical properties of vulcanizates made from heat-treated (and remilled) and benzidine stocks from those of untreated stocks almost certainly results from a greater breakdown of carbon structure during mixing. The effect of benzidine in decreasing the plasticity of unvulcanized rubber has been referred to, and it is now suggested that this property is related to its ability to promote decatenation by increasing the effect of shear during milling. There is a further possibility that benzidine, together with certain other amines, might act by increasing the tendency for carbon particles to adsorb rubber molecules. It may be imagined that the viscous forces developed in the nip of the mill are transmitted to chains of carbon particles by attachments between rubber molecules and the particles of carbon; otherwise rubber molecules tend to slide over the carbon chains without the attachments between the particles being broken. Milling breaks down the chains if the adsorptive forces between carbon and rubber are greater than the adhesive forces between carbon particles. The evidence suggests that both in benzidine-treated and heat-treated stocks more of the black is dispersed as individual particles than in untreated stocks, and the inference is that both treatments increase the attachments between carbon particles and rubber molecules.

One of the most striking effects of heat and benzidine treatment on the properties of the vulcanizates is the increase in rebound resilience. The inference is that the friction between carbon-to-carbon and carbon-to-rubber surfaces decreases as the number of discrete particles increases, and might be expected if such particles are attached to rubber molecules. The relatively poor tear strength of heat-treated, and particularly of benzidine heat-treated compounds, may be associated with the decreased structure. The effect of heat treatment on abrasion resistance is small, a slight increase having been noted[12]. No significant change in abrasion has been found to accompany the benzidine treatment.

This investigation has strengthened conclusions from previous work reported by one of the authors[12,13,14,15] that changes in carbon structure, though influencing the properties of rubber vulcanizates, are secondary factors in the mechanism of carbon reinforcement. It seems evident that the arrangement of the particles can be considerably modified without the reinforcing properties being greatly changed. It would appear that increasing the carbon-rubber attachments at the expense of the carbon-carbon attachments influences some properties positively and others negatively.

SUMMARY AND CONCLUSIONS

The properties of rubber vulcanizates containing channel black can be modified either by heat treatment under certain conditions of the rubber-carbon stock or by addition to the stock of small quantities of certain chemical substances, including benzidine. The effects of heat treatment and benzidine are to some extent additive, and it is shown by electrical resistance measurements that they are associated with changes in the configuration of the carbon particles in the rubber.

The resistivity of unvulcanized channel black-rubber stocks depends on the temperature and on any temporary stretching or flexing to which the rubber may have been subjected. Any change which causes increased carbon structure which may occur when the stock is heated is reversed when it is cooled and strained.

Remilling of rubber-black stocks results in an increased electrical resistance, due to a breaking down (decatenation) of chains of carbon particles. This effect is enhanced by previous heating of the stock or by incorporation of benzidine. Once the structure is broken down in this way there is no evidence that it can be formed again.

For these and other reasons the hypothesis that individual carbon particles flocculate in rubber by a mechanism such as Brownian movement of the particles is rejected.

It is suggested that the increased resilience of carbon-rubber vulcanizates following heat or benzidine treatment of the unvulcanized stock results from an increase of the carbon-rubber attachments at the expense of the carbon-carbon attachments.

APPENDIX

Experimental technique of resistance measurements.—Electrical contact with the samples was made by using aquadag to paste tinfoil contacts on to the rubber. The resistance of conductive rubbers was measured by a Taylor general-purpose meter, but for resistances greater than a megohm a condenser was either discharged or charged through the unknown resistance. By timing

the change in voltage of the condenser between suitably chosen values the resistance can be calculated (treatments of the charge and discharge of a condenser through a resistance may be found in text-books of electricity). In theses experiments the voltage on the condenser was measured by putting it on the grid of an electrometer valve and noting the change in anode current which it produces. Resistances between 10^6 and 10^{12} ohm were measured by discharging a condenser through them and those greater than 10^{12} ohm were determined by charging a condenser *via* the resistance using a high negative voltage (-200 v), which produces a rapid initial rate of charge even when the resistance is very high. Measurements of resistances greater than 10^{11} ohm tend to be variable and therefore somewhat unreliable, due to insulation leakage and surface moisture on the samples at low temperatures.

ACKNOWLEDGMENT

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THE EFFECT OF PILE BOMBARDMENT
ON UNCURED ELASTOMERS *

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INTRODUCTION

In the past numerous workers[1] have studied the behavior of simple hydrocarbons exposed to various kinds of ionizing radiations. Although a wide variety of experimental arrangements and techniques is described, remarkably similar effects were obtained by these workers. In fact, the results are so much alike that one is forced to conclude that for the same energy expenditures, electrons, deuterons, and alpha particles are roughly equivalent as regards chemical changes induced in gaseous hydrocarbons.

The essential facts are these:

(1) Gases always constitute one type of reaction product. These gases consist of H_2 and various saturated hydrocarbons. Practically no unsaturated products are found in the gas phase, even though the target material may be unsaturated. This is in sharp contrast to the results obtained from thermal and photochemical decompositions or when hydrocarbons are passed through an electric discharge. For example, Yeddanapalli[2] found that acetylene and ethylene are prominent products when methane is passed through a glow discharge tube.

(2) A certain amount of high boiling liquid (polymer), or in some cases a solid residue, is also formed in the presence of ionizing radiations. These products do show unsaturation and normally yield a structure close to (C_nH_{2n}). On extended irradiation, the gaseous phase becomes predominantly H_2; the remainder of the sample is converted to the liquid state. In fact, this behavior has led Lind to propose a radiation theory for the genesis of petroleum.

(3) The M/N yield (number of target molecules converted per ion pair) is approximately 2 for all saturated hydrocarbons which have been investigated. Unsaturated materials show an erratic behavior; C_2H_4 gives $M/N = 5$, for C_2H_2 the figure is 20, while for benzene vapor $M/N = 1$.

(4) In spite of the previous statement, the gaseous yield is much higher for saturated feed materials. As an example, Schoepfle and Fellows[3] obtained the following yields of gaseous products when the liquids listed were subjected to

equal bombardments with 170-kev electrons:

Irradiated compound	Gas evolved (STP)
n-Octane	48.3 cc.
Diisobutylene	20.8
Benzene	2.2

(5) A corollary to (3) and (4) states that normally much more polymer product is produced when the bombarded material is unsaturated. This can be confirmed by reviewing the following data taken from Burton's report MDDC 17. Here G denotes the number of molecules of target material converted to (a) gas or (b) polymer, per 100 electron volts absorbed. When liquids are under investigation, as was the case here, it is considered more proper to report results in terms of G rather than M/N, since the ionizing potential of a liquid is not easily determined. Interestingly enough the total conversion per 100 ev. is the same for both materials. However, in one case the major product is gaseous, whereas for cyclohexene, polymerization is the predominant reaction.

Target material	G gas	G polymer
Cyclohexane	4.0	1.2
Cyclohexene	1.0	4.2

No one has yet succeeded in explaining satisfactorily all the previous facts. Early in the game Lind introduced his famous cluster theory. In this theory the first step consists of ionization. For ethane bombarded with α's he suggests:

$$C_2H_6 \xrightarrow{\alpha} C_2H_6{}^+ + e^-$$
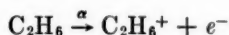
The positive ion then attracts a neutral ethane molecule to itself. This constitutes the cluster. (For acetylene the $C_2H_2{}^+$ ion is assumed to attract $19C_2H_2$ molecules in order to justify $M/N = 20$.) The second step can be written:

$$C_2H_6{}^+ + C_2H_6 \rightarrow (C_2H_6)_2{}^+$$
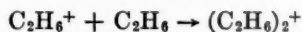
The third step comprises neutralization of the cluster by a negative ion or electron. In the ethane case Lind found H_2, CH_4, C_2H_6, C_3H_8, and C_4H_{10} in the gas phase after bombardment. To explain these findings, he assumes that on neutralization the cluster can break up in at least three ways:

1. $(C_2H_6)_2{}^+ + e^- \rightarrow C_4H_{10} + H_2$.
2. $(C_2H_6)_2{}^+ + e^- \rightarrow C_4H_8{}^* + 2H_2 + xC_4H_8{}^* \rightarrow (C_4H_8)_x$ polymer

The butene is said to be formed in a nascent state, and immediately x molecules of butene react to form a molecule of liquid. This explains why no unsaturates appear in the gas phase.

$$3. \quad (C_2H_6)_2{}^+ + e^- \rightarrow CH_4 + C_3H_8$$
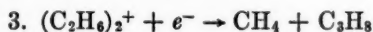
Reactions (1) and (2) correspond to condensation and dehydrogenation plus polymerization, whereas (3) represents a cleavage. Had we considered ethylene instead of ethane, the cluster would have consisted of 5 molecules. On neutralization of this cluster a majority of the products would be unsaturated, which on Lind's picture requires that they immediately polymerize. This, then, explains why unsaturated materials yield more polymer and less gas.

The cluster theory has proved too naïve for many people; including Eyring, Hirschfelder, and Taylor[4]. They prefer to speak of chain reactions initiated by atoms and free radicals. In fact they partially discount the effects of ionization in radiation chemistry, saying that at least half of the initiating free radicals or atoms are formed by molecular dissociation from excited (not ionized) states. The other half are thought to be formed when the ions are neutralized. Even Lind admits that the cluster theory has to be abandoned for the case of radiochemical synthesis of HCl from H_2 and Cl_2 where M/N > 1000. The free radical-atom theory has been applied to only a few relatively simple radiochemical reactions, such as the conversion of *ortho*-H_2 to *para*-H_2 by α-particle bombardment and the synthesis or decomposition of HBr. Apparently too little is known about the excitation, ionization, and general ionic behavior of hydrocarbon fragments to attempt a detailed analysis of such experiments.

TABLE I

COMPOUNDS STUDIED

	1	2	3	4	5
Smoked sheet	100	100		100	
Polyisobutylene			100		100
EPC black		30	30	30	30
Ammonium borate				26.4	26.4

	6	7
Butyl rubber	100	
Polyisobutylene		100
Carbon black	50	50
Zinc oxide	5	5
Stearic acid	1	1
Sulfur	2	2
Mercaptobenzothiazole	0.5	0.5
Tetramethylthiuram disulfide	1	1
Ammonium borate	26.4	26.4

In the literature one finds few articles reporting the effects of radiations on unvulcanized elastomers. There are two German papers relating to the effect of the silent discharge on rubber solutions. However, these are not particularly helpful because they relate quite opposite results. Fromandi[5] finds a sharp decrease in solution viscosity, iodine number, molecular weight, and softening point of both natural rubber and polyisoprene[6].

Hock and Leber[7], working at a later date in the same laboratory, found equally large increases in these same properties. The latter workers explain Fromandi's results as due to small traces of oxygen present in the reactor system. The oxygen would be converted to ozone in the discharge and then degrade the rubber chains.

Newton[8] claims vulcanization of thin rubber films by subjecting them to short (20–25 sec.) bombardments with 250 kb cathode rays. He reported that the samples showed good tensile strength, were swelled but not dissolved by benzene, and exhibited excellent resistance to accelerated aging tests. No tensile figures are included, however, so it is rather difficult to assess these results quantitatively.

With this meager background to build on, we will now describe the experiments performed in the nuclear pile at Oak Ridge on natural rubber, Butyl rubber, and PIB.

COMPOUNDS USED

The compounds used are given in Table I. Natural rubber was used in 1, 2, and 4. Stock 1 is smoked sheet as received at the factory. All other compounds were mixed on a laboratory mill and sheeted out to a thickness of 0.1 inch. Thirty parts of a typical reinforcing black were added to 100 parts of smoked sheet in 2, and 26.4 parts of ammonium borate equivalent to 5 parts boron were added to the Compound in 4.

Compounds 3 and 5 are polyisobutylene compounds to be compared with the corresponding natural rubber compounds 2 and 4.

Compounds 6 and 7 were mixed to determine if a polyisobutylene stock can be cured like a Butyl stock after irradiation. Compound 6 is a typical Butyl stock except for the addition of ammonium borate. Curing ingredients—zinc oxide, stearic acid, sulfur, mercaptobenzothiazole, and tetramethylthiuram disulfide—are added to the Butyl rubber, carbon black, and ammonium borate. Compound 7 is to be compared with 6, polyisobutylene in 7 replacing Butyl rubber in 6.

EXPERIMENTAL PROCEDURE

Small pieces of stock, about 2×2 inches, were cut out and inserted in a "rabbit". The rabbit is a small cylindrical box which fits snugly inside a pneumatic tube and is driven through the tube by tank carbon dioxide. The pneumatic tube extends to the center of the pile. Cooling air is drawn past the tube, so the temperature of the rabbit seldom exceeds 30° C, which eliminates the possibility of thermal effects on the samples. The time required by the rabbit to reach the center of the pile from outside is only 2 seconds, so the exposure can be precisely controlled. After exposure, Goodrich plasticity[9] and iodine number[10] were determined for representative samples. These data are summarized in Tables II and III.

TABLE II

GOODRICH PLASTICITY (70° C) FOR VARIOUS EXPOSURES IN CLINTON PILE

Exposure→ stock ↓	0	1'	4'	16'	32'	60'	120'
1	3				4		
2	36				27		
3	5				13		
4	21	18	15	6	4	4	3
5	14	19	33	62	70		
7 (Uncured)	15						
7 (Cured)	16				80	89	

TABLE III

UNSATURATION IN STOCKS AFTER VARIOUS EXPOSURES IN CLINTON PILE. Smoked sheet is 100 per cent

Exposure→ stock ↓	0	4'	32'	120'
1	89		82	
2	95		97	
3	1		0.5	
4	98	96	98	95
5	8	8	5	

The unsaturation data are not very illuminating. In general, pile bombardment of natural rubber seems to decrease its unsaturation, although this trend is reversed in Compound 2. It is somewhat disturbing that Samples 3 and 5 should show such different iodine numbers when they are identical except for the ammonium borate content of 5. About all that can be said with regard to these latter samples is that they show no increase in unsaturation as a result of bombardment.

EXPERIMENTAL RESULTS

NEUTRON INTENSITIES

In Samples 1, 2, 3 any effects noted, either physical or chemical, can be assigned to:

(a) Ionization produced by fast electrons resulting from γ-radiation.

(b) Secondary ionization by fast neutrons.

(c) $C-C$ and $C-H$ cleavage by fast neutrons.

(d) $C-H$ cleavage by H capture of slow neutrons due to recoil from γ-ray emitted.

Calculations indicate that processes (a) and (b) are about equally effective in breaking chemical bonds, while (c) and (d) are negligible by comparison.

From the dearth of previous work in this field, it is impossible to predict which of the four processes listed in the Introduction predominates here. However, it is interesting to speculate briefly concerning the relative bombardment times required to bring about certain changes in the elastomer, making in turn the hypothetical assumption that every broken bond acts to produce the particular change desired. The changes to be effected are:

1. Sufficient $C-C$ cleavage to halve the molecular weight (decomposition). (45×10^{18} $C-C$ bonds must be broken per gram of rubber if the mole weight is 140,000.)
2. Sufficient cross-links to equal a sulfur cure (condensation or polymerization). (9×10^{19} cross-links needed per gram to assure 1 cross-link per 100 C_5H_8 units.)
3. Creation of sufficient double bonds in PIB to equal the unsaturation present in Butyl rubber (dehydrogenation) (1.8×10^{20} double bonds needed to give 2 per cent unsaturation; where natural rubber has 100 per cent unsaturation).

Of course if the three processes are equally probable, degradation of the elastomer predominates in every instance.

Even if processes (2) and (3) are highly favored, calculations imply that the bombardment times to achieve the desired end effects are too long to arouse much technical interest. To accelerate the ionization effects, we prepared Stocks 4, 5, 6, and 7 containing 5 parts boron per 100 of elastomer (added as ammonium borate).

The slow neutron reaction $B^{10} + n^1 \rightarrow Li^7 + He^4$ is a very prolific one. Total K.E. of the Li^7 and He^4 averages 2.4 Mev per event, and essentially all this appears as excitation and ionization. If we can believe previous radiation studies, the effects produced are identical with those for the nonboron stocks except in magnitude.

For equal bombardments we may anticipate an effect here some 80 times that deduced for the nonboron samples. Conversely, with boron present, we

might hope to achieve marked changes in times well within the range of technical interest.

RELATION BETWEEN PLASTICITY AND MOLECULAR WEIGHT

To evaluate the increased effects of the added boron, we need to know what the plastometer readings correspond to in terms of molecular weight. Apparently no such relation has been established for this instrument. Karrer, Davies, and Dietrich[9] plot Goodrich plasticity as a function of milling time for a batch of crepe rubber. In addition, Wildschut[11] has published a curve showing molecular weight *vs.* milling time for a crepe sample. If we make the rough assumption that these two samples underwent equal mastication, it is possible to obtain a curve relating Goodrich plasticity and molecular weight for crepe rubber. This curve is depicted as the inset portion of Figure 1. It would
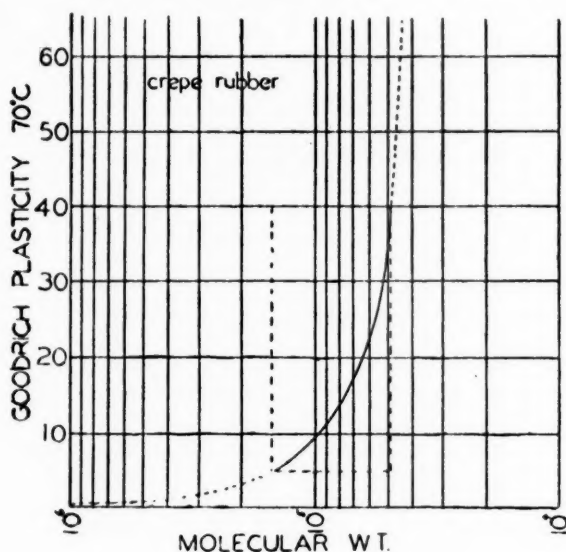
Fig. 1.

appear that the interpretation in terms of molecular weight should be limited to plasticity readings between 5 and 40. Although the curve is strictly applicable to crepe rubber only, we shall use it for our samples here in the absence of better information. Table IV records the molecular weights obtained in this manner.

TABLE IV

MOLECULAR WEIGHTS (X10⁻³) OF STOCKS AFTER VARIOUS EXPOSURES IN CLINTON PILE.
Values obtained from plastometer-viscosity curve.

Exposure → stock ↓	0	1'	4'	16'	32'
1	—				—
2	52	—	—	—	56
3	140	—	—	—	88
4	62	69	80	125	—
5	82	67	53		

Compound 2 reveals an increase in molecular weight from 52,000 to 56,000 after 32 minutes bombardment, or a rate of $\frac{1}{4}$ per cent per minute. Compound 4 shows a 100 per cent increase in 16 minutes, which figures 6 per cent per minute. Thus the boron accelerates matters here by only 25-fold instead of the calculated 80 times.

Comparing the degradation induced in PIB, a 32-minute irradiation of 3 goes 75 per cent of the way toward halving the molecular weight. Roughly the same result is produced in 5 after 4 minutes in the pile. This implies a mere 8-fold enhancement due to boron, although on the basis of chains broken we should raise this to 14-fold since 5 starts at a molecular weight of 82,000 compared to 140,000 for 3. In any event it seems clear that in neither instance does boron fully live up to expectations. It may be that the heavier ionization left in the wake of an alpha particle (compared to that from a proton or electron) leads to considerable recombination within the ionization column, though this does not appear to be the case with gaseous targets.

EXPLANATION OF EXPERIMENTAL FINDINGS

How does one explain the fact that natural rubber increases in molecular weight under pile bombardment while PIB is degraded? The explanation must lie with the unsaturation in natural rubber. The authors suggest that the first two steps, ionization and neutralization, are similar for both materials. If ionization occurs at the expense of a valence electron belonging to a chain carbon, cleavage of the chain probably takes place. On neutralization, free radicals are generated. In natural rubber these radicals are able to initiate chain reactions involving double bonds. Apparently the cross-linking established in this way more than compensates for the broken chains. With PIB no chain reaction can be effected, so the end result has to be degradation.

In view of the large amount of H_2 found in previous radiation experiments involving hydrocarbons, it seems inevitable that some unsaturation would be induced in both types of elastomer. The apparent decrease in iodine number for natural rubber with radiation time is not unexpected in view of the chain reaction feature suggested above. The absence of an increase in iodine number for PIB, however, is somewhat disturbing. It is true that the unsaturation introduced in PIB would be only a few per cent at most, and the iodine method
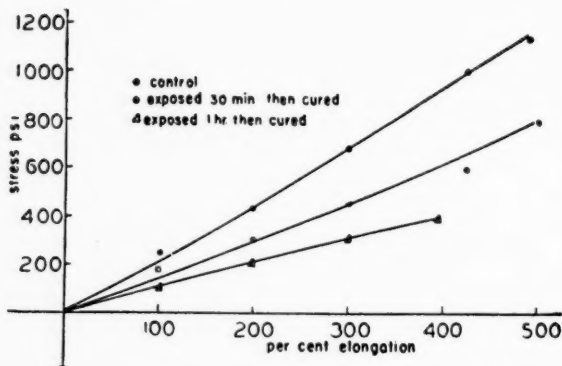
FIG. 2.—Effect of pile bombardment of Butyl rubber stock.   Cure 80 min., 307° F.

does not seem to be entirely satisfactory.   Because of this uncertainty we formulated Compound 7, and tried to cure it after extended irradiation in the pile.   As is evident from Table II, this effort did not succeed.   If any unsaturation had been created it was certainly overshadowed by the cleavage. This is further borne out by tests on 6, a Butyl compound.   Figure 2 depicts the effect of pile bombardments on the stress-elongation curve of the cured material.   It is evident that the degradation effects persist even after cure.

STUDIES WITH VULCANIZED ELASTOMERS

Butyl Rubber

It was deemed of interest to determine if pile bombardment would degrade a specimen of vulcanized Butyl rubber as much as it did the uncured stock. Therefore a cured sample (80 minutes at 307° F) of Compound 6 was exposed to the pile as before, for a period of 1 hour.   A subsequent tensile test repeated within experimental error the curve of Figure 2 for the sample which had been bombarded for an hour before curing.   Apparently the degradation induced is essentially independent of the state of vulcanization.   Fragments from this sample were subjected to three passes through a laboratory mill.   This treatment resulted in a well knit material which might be classified as Butyl rubber reclaim.   This could be taken as superficial evidence that the pile has possibilities as a reclaiming agent for Butyl rubber.

Natural Rubber

It was also decided to ascertain the effect of pile radiations on cured natural rubber.   Compound No. 8 was chosen for this test and given a cure of 80 minutes at 280° F.   The resulting stress-elongation curve is presented in Figure 3a.   The low tensile strength is accounted for by the poor dispersion of the borate in the compound.   A sample of this cured compound was likewise subjected to 1 hour in the pile.   The curve of Figure 3b, illustrates the stress-
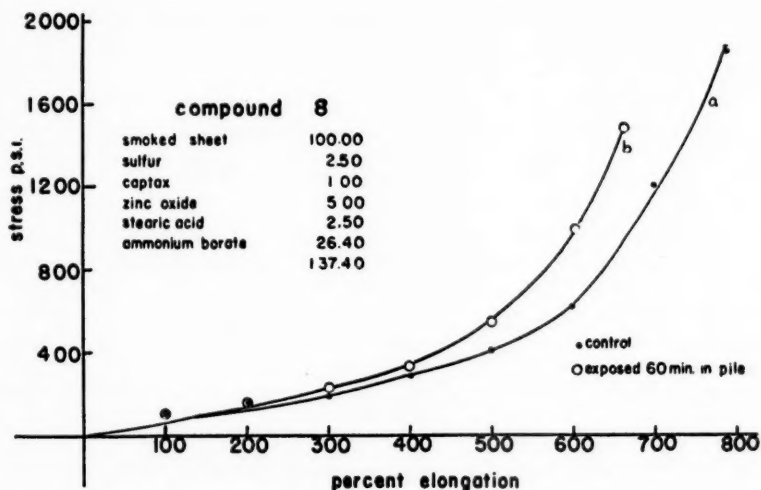
FIG. 3.—Effect of pile bombardment on cured natural rubber stock.   Cure 80 min., 280° F.

elongation characteristics after bombardment.   It is clear that the modulus has increased appreciably, while a corresponding decrease has occurred in the tensile strength.   This is typical of accelerated rubber stocks thst have been subjected to a long overcure.   From the weak vulcanizing effect of a 1-hour pile exposure on uncured rubber, it seems impossible to account for the present change as a conventional overcure phenomenon.   It may be true that the sulfur linkages that are already present here in some way suppress the degrading effects of pile bombardment, thus allowing the vulcanizing tendencies to be more pronounced.   At the moment there is insufficient evidence to permit speculation as to the mechanism for this suppression.

ACTIVITY OF IRRADIATED SPECIMENS

Specimens of 1, 2, 3, 4, and 5 were tested for radioactivity several days after irradiation. $\frac{1}{2} \times \frac{1}{2}$-inch specimens from each irradiated piece were placed in a standard position below the 10 mg. per sq. cm. mica window of the Geiger tube.   The natural rubber Compounds 1, 2, and 4 had a small but measurable activity.   The PIB compounds showed practically no activity.   Activities are given in Table V.   The background for the counting tube used was 60

TABLE V
RADIOACTIVITY INDUCED IN STOCKS DURING PILE BOMBARDMENT

Irradiation time (min.)	Net activity counts per minute	
	No. 4	No. 5
1	19	13
2	13	13
4	38	6
8	64	6
16	77	19
32	218	6
60	460	—
120	730	—

counts per minute.   The activity in natural rubber is doubtless accounted for by its mineral content.

SUMMARY

Previous work on the effects of ionizing radiations on hydrocarbons has established that four competitive processes are usually operative: (1) dehydrogenation, (2) condensation or polymerization, (3) hydrogenation (action of nascent hydrogen on any unsaturated matter present), (4) decomposition (C-C cleavage).   The chain reacting nuclear pile offers an ideal means for subjecting relatively thick samples of matter (such as rubber) to uniformly high concentrations of radiation.   Such studies on natural rubber, Butyl rubber, and polyisobutylene allow one to draw the following conclusions.   1. Uncured natural rubber undergoes a slight curing action when exposed to pile radiations. 2. Polyisobutylene samples are appreciably degraded by pile radiations. 3. The same effects as noted in (1) and (2) are greatly enhanced by secondary alpha particles, produced by an (n, α) reaction on boron[10] (milled into the elastomer).   However, even a 2-hour bombardment of natural rubber yields a product greatly inferior to sulfur vulcanizates.   4. Pile bombardment does not introduce measurable unsaturation in polyisobutylene and decreases the unsaturation in natural rubber but slightly.   5. A typical Butyl rubber stock

is permanently degraded by pile irradiation, showing on cure reduced tensile strength compared to that of a control sample. 6. Natural rubber shows a weak but measurable radioactivity days after bombardment, probably because of its mineral content. Polyisobutylene is not appreciably active.

ACKNOWLEDGMENT

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STUDY OF THE REACTION OF BUNA RUBBERS WITH ALIPHATIC THIOLS *

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INTRODUCTION

The relative proportion of 1,4- *versus* 1,2-addition of diene units and the elucidation of the partial structure of polymers and copolymers of butadiene have been investigated by various chemical and physical methods, such as ozonolysis[1], perbenzoic acid oxidation[2], potassium permanganate oxidation[3], and infrared absorption[4]. The work presented in this paper was undertaken in an attempt to obtain further information regarding the structure of butadiene polymers and copolymers by studying the reaction of these polymers with aliphatic thiols.

The reaction of thiols with unsaturated compounds, including natural and synthetic rubbers, is not new. Posner[5], Gunnar, Axberg and Holmberg[6], Hoag and Eichwald[7], Kharasch, Read and Mayo[8], Jones and Reid[9], Cunneen[10], and others have treated thiols with various types of unsaturated compounds. Holmberg[11] treated natural pale crepe rubber with thioglycolic acid, and more recently, Kolthoff and coworkers[12], and Marvel and coworkers[13] studied the reaction of aliphatic thiols with butadiene polymers and copolymers in latex form.

From a preliminary study of the reaction of thiols with model compounds, it was found that ethylenic bonds in conjugated, vinyl, terminal butenyl, and in closed ring structures add thiols readily, while internal, nonconjugated ethylenic bonds react at a relatively slower rate. Thioglycolic acid adds to simple olefins more vigorously than *n*-aliphatic thiols. Since this paper was originally submitted, Cunneen[14] reported the reactions of unsaturated hydrocarbons and various thiols. An apparent order of reactivity was found to be cyclohexene > dihydromyrcene > squalene > rubber; and for the thiols, thioglycolic acid > thiophenol ∼ isopentanethiol. It is evident that the ease with which an ethylenic bond can add thiols depends, in part, on the structural unit retaining the double bond.

It is probable that diene polymers contain several types of ethylenic bonds, but from ozonolysis data[1] it must be concluded that a major portion of these bonds results from either 1,2- or 1,4-addition of butadiene units to the polymer chains. These two types of ethylenic bonds should exhibit different rates of thiol addition, and the determination of the proportion of thiol-reactive units in the polymer chains should represent a measure of the percentage of ethylenic bonds present as side vinyl groups. Ethylenic bonds in structures formed by intramolecular cyclization reactions should likewise be thiol reactive. Obviously thiol-addition reactions do not show complete selectivity for side vinyl

groups, but it is very probable that thiol reactive structures other than the side vinyl groups represent only a very minor portion of the total unsaturation of the butadiene polymers.

This paper records the reaction of thioglycolic acid and n-aliphatic thiols of C_2 to C_{16} chain length with diene polymers, and the reaction of thioglycolic acid and a n-C_{12} thiol with model compounds. Polymer-thiol reactions were effected in solution, mass and in latex form at various temperatures, in the presence of air, or in the presence of additives which were evaluated as catalysts. The experimental data indicate a pronounced difference in the rate and extent of thiol addition by the various diene polymers, and the difference in rate and extent of addition has been utilized in estimating the relative proportion of external and internal ethylenic bonds in the polymer chains.

EXPERIMENTAL

MATERIALS

Polymers.—The polymers used in studying the polymer–thiol reactions were natural rubber, polyisoprene, polybutadiene, and copolymers of butadiene and acrylonitrile, butadiene and styrene, and butadiene and alpha-methyl-para-methylstyrene. Both emulsion and sodium catalyzed polymers of butadiene were used, but in all other cases, emulsion polymers and copolymers were employed. The emulsion polymers were prepared by the standard technique. The polymerization reactions were discontinued when 75 per cent of the monomers were converted to polymer. The latices were freed of unconverted monomers by steam stripping under a pressure of 50–60 mm. Polymers required for solution and mass reactions were obtained by coagulating the stripped latices with 99 per cent isopropyl alcohol, followed by water washing and drying at 175° F. No attempt was made to fractionate the resulting polymers, or to free them of any developed peroxide materials.

Thiols.—Thiols of C_2 to C_4 chain length were obtained from Eastman Kodak and were used after distillation. Thioglycolic acid was first dried by removing the water as a benzene azeotrope before distilling under vacuum. Normal thiols of C_8 to C_{16} chain length were of research grade from the Connecticut Hard Rubber Company. These thiols were used directly without further purification. Sharples 3B thiol was used after distillation.

Procedure.—A modification of the procedure used by Holmberg[11] was used in effecting the reaction of various polymers with thioglycolic acid. A 5 percent solution of polymer in benzene was placed in a flask and agitated while a calculated amount of dry thioglycolic acid was added slowly to the solution at room temperature. The reactants were allowed free access to air throughout the course of the reaction. With butadiene polymers and copolymers the reaction was exothermic, and after a short time the solution became cloudy and an insoluble layer separated. The separated product was solubilized by the addition of n-hexanol and the reaction continued. Samples were withdrawn periodically for analysis. The polymer–thioglycolic acid reaction products were purified by water washing the benzene–n-hexanol solutions until no further test for free thioglycolic acid could be obtained by titration with 0.1 N iodine solution. The solvents were then removed by heating the solutions on a steam-bath under high vacuum. The reaction products were further dried in a vacuum oven at 70°. Sulfur analyses of the products were obtained by combustion in a Parr bomb.

Polymers in latex form were treated with thiols in 2-oz. and one-quart glass reactors, which were charged to varying levels and then agitated in a thermostatic bath at 50° for varying periods of time. The amount of thiol employed corresponded to a 100 per cent excess over the amount theoretically required for complete double-bond saturation. Several conditions were employed wherein the free space of the reactors was flushed either with nitrogen, air, or pure oxygen; and the amount of persulfate in the systems was varied. The polymer–thiol reaction products were isolated from the emulsions by coagulating in an excess of 99 per cent isopropyl alcohol. The products were thoroughly washed in fresh portions of alcohol and then dried in a vacuum oven at 70°.

Mass reactions of dry polymers and thiols were carried out under essentially the same conditions employed by Jones and Reid[9] in their study of the reaction of thiols with unsaturated compounds. The dry polymer was dissolved in the desired thiol, two mols of thiol were used per mole of diene in the polymer. The solutions were agitated in a glass reactor, sealed from the atmosphere without displacing the air in the reactor, at 180–200° for varying periods of time. Samples of the reaction mixture were removed at intervals for purification and analysis. The polymer–thiol reaction products were isolated by coagulating the reaction mixture with a large volume of 99 per cent isopropyl alcohol followed by repeated dissolution of the mass in petroleum ether and coagulation until the mixed solvents showed no trace of free thiol as determined by titration with 0.1 N iodine solution. The purified reaction mass was stripped of solvents and moisture under vacuum at 80°.

Calculations.—The calculation of the percentage of double bonds saturated by a particular thiol is based on the sulfur content of the reaction product, molecular weight of the thiol, and the unsaturation value of the polymer expressed as Wijs number. It is assumed that the total sulfur of the reaction product minus the sulfur value of the original polymer represents the total sulfur introduced into the polymer by the additive fixation of the thiol. The percentage of double bonds saturated was calculated from the expression:

$$\% \text{ D.B. saturated} = \frac{2.54 \times 10^6 \, (\% \, Sa - \% \, Sp)}{[3200 - (\% \, Sa - \% \, Sp)(\text{Mol. wt. RSH})]I_{2p}}$$

where

Sa = % Sulfur of the reaction product
Sp = % Sulfur of the original polymer
I_{2p} = Wijs number of original polymer.

RESULTS AND DISCUSSION

Reactions of thiols and unsaturated compounds.—In determining the relative reactivities of various types of ethylenic bonds with aliphatic thiols, model compounds were employed which possessed either terminal or internal unsaturation. The results of these experiments, given below, indicate that compounds possessing terminal methylene groups or double bonds in closed ring structures add thiols vigorously, whereas internally located double bonds react very slowly with thiols.

Oleic acid (0.1 mole), free of linoleic and linolenic acids, and thioglycolic acid (0.1 mole) when combined in benzene (50 cc.) at room temperature did not produce an exothermic reaction. The product, isolated from the reaction mixture after standing at room temperature for ten days with access to air,

contained 6.60 per cent sulfur (calcd. for $C_{20}H_{38}O_4S$: S, 8.53 per cent). By treating linoleic acid (0.1 mole) and thioglycolic (0.2 mole) in the manner described above, a yield of 40.3 grams of adduct and unreacted linoleic acid was obtained after 29 days' reaction time at room temperature (calcd. amount of adduct 46.44 grams). On the other hand, when one-tenth molar proportions of 10-undecylenic acid and thioglycolic acid were combined as above, a highly exothermic reaction resulted. The solid, crude product, isolated from the water-washed benzene solution, contained 12.36 per cent sulfur (calcd. for $C_{13}H_{24}O_4S$: S, 11.58 per cent).

Cyclohexene (0.1 mole) and thioglycolic acid (0.1 mole) also reacted exothermally in benzene in the presence of air. The product, after being water washed and dried under vacuum and undistilled, showed a sulfur content of 20 per cent (calcd. for $C_8H_{14}O_2S$: S, 18.4 per cent). This reaction was described by Cunneen[10].

Molar proportions of 10-undecylenic acid and n-dodecanethiol reacted exothermally in benzene solution in the presence of air. This reaction was less vigorous than when thioglycolic acid was used. The solid reaction product after a single crystallization from benzene showed a sulfur content of 8.20 per cent (calcd. for $C_{23}H_{46}O_2S$: S, 8.30 per cent).

Reaction of polymers.—An emulsion copolymer of butadiene and styrene, prepared from an initial feed ratio of 78 parts of butadiene and 22 parts of styrene by weight, reacted exothermally with thioglycolic acid after a few minutes of contact. Reaction products isolated after 3, 25, 45, 70 and 144 hours, showed 47, 42, 38, 43 and 42 per cent double bond saturation values, respectively. These data indicate that the reaction is exceedingly rapid and apparently reaches a saturation value corresponding to about 38–47 per cent double-bond saturation. Under the same conditions, a copolymer prepared from an initial feed of 74 parts of butadiene and 26 parts of acrylonitrile, and a polybutadiene prepared by sodium catalysis, reacted exothermally with thioglycolic acid and after twenty-five hours the products were isolated and showed 42 and 39 per cent double-bond saturation values, respectively. Natural smoked sheet, purified by acetone extraction, solution, and precipitation, showed no exothermic reaction with thioglycolic acid in benzene solution under the same conditions. After one month the isolated product showed a sulfur content of 7.04 per cent, which corresponds to 18.8 per cent double-bond saturation. Cunneen[10] found but a slight reaction between natural rubber and thioglycolic acid under peroxidic conditions and high vacuum. The above experiments emphasize a pronounced difference in the reaction rate between thiols and butadiene polymers and natural rubber. The difference in reaction rates is undoubtedly due to the presence of different double-bond structures in the respective polymers.

The double-bond saturation values obtained for butadiene polymers and natural rubber, treated in latex form with thiols, also indicate a pronounced difference in the reaction rate and the extent of reaction. Emulsion polymer latices, containing equivalent amounts of residual potassium persulfate catalyst, when sealed in reactor vessels with an excess of ethanethiol in such a manner that the vessel was flushed with nitrogen and thiol vapor, reacted with a definite and reproducible amount of thiol. This addition proceeded rapidly during the first three to six hours of reaction time at 50°, and reached a limiting value which was unique for the type of polymer being treated. These observations are illustrated by the data of Table I. It will be noted that polymers and

TABLE I

REACTION OF ETHANETHIOL WITH EMULSION POLYMERS IN
AIR-FREE SYSTEMS

Latex	Reaction time (hrs. at 50°)	Percentage of double bonds saturated
Buna-S	23	25
Sample A(1)	46	27
Sample B(2)	45	23
Buna-N (3)	2	9
	6	12
	48	12
Polybutadiene	3	10
	19	13
	65	14
Polyisoprene	3	3
	47	4
Natural rubber	20	2
	64	2

Weight-percentage monomers in polymerization charge:

(1) Butadiene, 78; styrene, 22
(2) Butadiene, 75; styrene, 25
(3) Butadiene, 72; acrylonitrile, 28.

copolymers of butadiene showed a relatively greater proportion of double bonds reacted than emulsion polyisoprene or natural rubber in air-free systems containing equivalent amounts of persulfate catalyst.

The effect of oxygen and peroxides on the rate and extent of ethanethiol addition to Buna-N polymers was followed by effecting the reactions in vessels charged to varying levels. The charged reactors were flushed with air before sealing. It will be noted from the results presented in Table II that when the reactors were completely filled, the amount of ethanethiol which added to the polymer double bonds was the same as when oxygen had been flushed from the

TABLE II

REACTION OF BUNA LATICES WITH C_2–C_4 THIOLS IN
THE PRESENCE OF AIR

Latex	Charging volume[a]	RSH	Reaction time (hrs. at 50°)	Percentage of double bonds saturated
Buna-N[b]	20	Ethyl	20	39
Sample A[c]	28	Ethyl	3	27
	28	Ethyl	17	40
	28	Ethyl	43	40
	35	Ethyl	20	36
	63	Ethyl	20	31
	87	Ethyl	20	17
	100	Ethyl	20	12
Sample B[d]	28	Ethyl	20	40
	100	Ethyl	20	13
Sample C[e]	28	Ethyl	20	40
	100	Ethyl	20	12
Buna-S[f]	30	Ethyl	48	45
	30	n-Propyl	48	35
	30	n-Butyl	48	41

[a] Percentage of volume of 2-oz. reactor occupied by latex and thiol. [b] Monomer feed ratio, weight per cent: butadiene, 74; acrylonitrile, 26. [c] Contained 0.30 parts $K_2S_2O_8$ on monomers in charge. [d] Contained 0.15 parts $K_2S_2O_8$ on monomers in charge. [e] Contained 0.60 parts $K_2S_2O_8$ on monomers in charge. [f] Monomer feed ratio, weight per cent: butadiene, 75; styrene, 25.

systems. However, when the amount of free air space of the reactors was increased, the amount of thiol reacting with the polymer also increased, apparently approaching a limiting value of 35–45 per cent double-bond saturation. This saturation value did not change appreciably as a result of a prolonged reaction time, increased or decreased potassium persulfate concentrations used in the original polymerization charge, or by substituting n-propanethiol or n-butanethiol for ethanethiol. Further, it was observed that flushing the reactors with oxygen instead of air, or the addition to the reaction charge of 0.05 part of benzoyl peroxide, based on the polymer, did not affect the extent of thiol addition to the polymer. These data indicate that the reaction of thiols with Buna rubbers in latex form is catalyzed by oxygen, and the extent of double-bond saturation is of the same order of magnitude as was found when this polymer reacted with thioglycolic acid.

The data presented in Table III relate to the C_8 to C_{16} chain length thiol saturation values for polybutadiene, butadiene–styrene, and butadiene–μ–methyl–p-methylstyrene copolymers. The reactions were effected in mass at high temperatures. The data do not include the reaction rates, but only

TABLE III

MASS REACTIONS

| RSH | Percentage of double bonds saturated for polymer | | |
	A	B	C
n-C_8	41	..	52
n-C_{10}	44	..	56
n-C_{12}	47	42	42
n-C_{14}	35	42	36
n-C_{16}	40	41	48
3B	Gelled	Gelled	..

A, Polybutadiene. B, Butadiene, 50; styrene, 50; weight-per cent composition. C, Butadiene, 43.5; α-methyl-p-methylstyrene, 63.5; weight-per cent composition. 3B, Sharples 3B (tertiary) thiol.

summarize the values obtained during reaction times in which reaction apparently ceased. Although it was observed that the rate of thiol addition varied, the final polymer double-bond saturation values were of about the same order of magnitude. Sharples 3B thiol gave rise to gel polymers of low sulfur contents under the same reaction conditions.

The selectivity of the mass reaction at elevated temperatures appears to be overcome when a continuous stream of air is passed through the reaction mixture. Under such conditions, 75 per cent of the double bonds in a butadiene–styrene copolymer were saturated by a normal thiol of C_{14} chain length. The presence of volatile reaction products possessing an odor suggestive of aldehydes would indicate that under such drastic conditions the polymer was degraded.

In further experiments, polybutadiene reacted in mass with Lorol thiol in the presence of possible activating agents at various temperatures to determine whether the time of the reaction could be decreased, and whether activating agents have any effect on the selectivity of the reaction. Piperidine, zinc dibutyldithiocarbamate, anthraquinone, benzoyl disulfide, sulfur, and benzoyl peroxide were evaluated in concentrations of 2 to 10 per cent, based on the polymer, at temperatures of 75 to 180° for varying periods of time. Piperidine and anthraquinone exhibited an activating effect, but the extent of polymer double-bond saturation was unaltered.

Based on the partially known structure of butadiene polymers and co-polymers and on the vast difference in the rate at which vinyl and internal ethylenic bonds add thiols, it would appear that the 38 to 47 per cent of ethyl-enic bonds which added thiols readily are probably those derived from 1,2-addition of butadiene units to the polymer chains, or those arising from 1,2-addition and intramolecular cyclication reactions.

The saturation values obtained by the reactions between various types of thiols and butadiene polymers are in fair agreement in spite of a wide range of reaction conditions.

If it is assumed that the polymer double bonds which added thiols readily are those present in side vinyl groups, then the thiol saturation values found are in fair agreement with the value of 48 per cent for a butadiene–styrene copolymer as determined by potassium permanganate oxidation[3], and 34.5 and 42.8 per cent as determined by ozonolysis[14] for a butadiene–styrene and a sodium catalyzed polybutadiene, respectively. The thiol saturation values are not, however, in full agreement with those found by perbenzoic acid oxidation whereby emulsion butadiene–styrene copolymers showed 1,2-values of 27 and 20–22 per cent[2], while sodium catalyzed polybutadiene showed 58 per cent[15], side vinyl groups.

SUMMARY

Thioglycolic acid added exothermally to butadiene polymers and copolymers in benzene solution under mild conditions to give apparent double-bond saturation values of 38 to 47 per cent. When the same polymers reacted with aliphatic thiols of C_2 to C_{16} chain length, in mass or latex reactions, saturation values were obtained which were in accord with those found by thioglycolic acid addition.

It is suggested that the double bonds in butadiene polymers and copolymers which were readily saturated by the above thiols are predominately those present in the polymer chains as vinyl side groups.

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STEAM AND RADIO-FREQUENCY CURING
OF NATURAL RUBBER *

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The object of this investigation was to compare the resulting vulcanizates when natural rubber is cured in a conventional steam-heated mold and when it is cured by dielectric losses at radio frequencies under identical time-temperature conditions. In practice it is of course recognized that dielectric heating offers many advantages in speeding up heating processes through its inherent ability to heat uniformly throughout the mass, compared with relatively slower heating where heat is conducted in from hot surfaces. The purpose was, then, to determine if any appreciable difference in vulcanizates is obtained when identical conditions of time and temperature are artificially maintained by the two methods.

One series of tests was made on samples with different curing times at a fixed curing temperature; another series was carried out with a fixed curing time, with the temperature the independent variable. Finally a comparison was made with samples which had a curing cycle consisting of a gradually rising temperature during a relatively short curing time—that is, the type of temperature variation normally encountered in a radio-frequency cure when a constant radio-frequency field is imposed on a rubber load. The vulcanizates were evaluated physically by measuring their stress-strain relationships and ultimate tensile properties, electrically by their dielectric constant and loss factor-frequency dependence, and chemically by the amount of sulfur of vulcanization. No significant differences were observed in the rubber products cured by the two methods.

APPARATUS AND MATERIALS

To heat the rubber by radio-frequency voltage, it was placed in a suitable mold between condenser plates coupled to a 1200-watt commercial electronic heater. This radio-frequency generator utilized a pair of 833-A tubes in parallel in a Colpitts self-excited oscillator circuit. Matching to various impedance loads was accomplished by the scheme shown in Figure 1. Inductor L, consisting of ten turns of 0.1875-inch copper tubing, 2.5 inches in diameter by 4 inches long, was shunted across the oscillator tank to provide a transformer outside the heater unit where it could be conveniently tapped for matching purposes. Condenser C, $55\mu\mu$ farad, 7500-volt rating, was used as a coupling condenser and was omitted from the circuit in the case of high-impedance loads. The frequency used was between 17 and 18 megacycles per second depending on the characteristics of the load. This frequency was selected because it is near the absorption maximum of the rubber. During the initial rapid temperature rise, the field strength was of the order of 5.0 kv. per cm.; this was reduced to approximately 1.2 kv. per cm. to hold the temperature
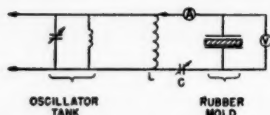
Fig. 1.—Diagram of mold circuit.

constant during the major part of the curing operation. These figures hold for the Mycalex mold whereas, for the higher loss Transite molds, only 1 kv. per cm. was used for the inductive heating period and 0.25 kv. per cm. held the temperature constant in the range of curing temperatures used.

A thermocouple radio-frequency ammeter and a General Electric Radio type 726A vacuum-tube voltmeter with potential divider were used to monitor the sample current and voltage.

The design of the rubber press for use in the electronic cures evolved into the practical form shown in Figure 2.

Celotex was used as a thermal insulator to minimize heat losses and consequent temperature gradients in the rubber slab. The 0.125-inch dielectric slabs on each side of the rubber were used to retain the rubber in the frame with-
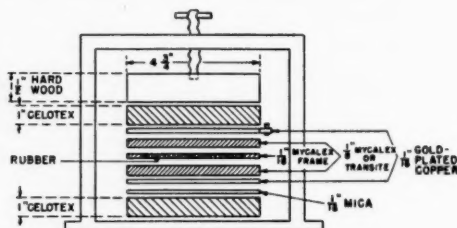
Fig. 2.—Radio-frequency rubber press.

out sticking to the electrodes; thereby, the mold was removable for easy filling and curing. These slabs also served as spacers to eliminate breakdown troubles between the electrodes, and, with the particular circuit used, the higher impedance load gained by wider electrode separation was favorable for optimum matching to the generator. The retainer mold for the rubber is shown in Figure 3.

To make all parts of the mold interchangeable, the flat Mycalex or Transite stock for the three parts of the old were racked and milled together to ±0.005 inch. To avoid breakage, the 0.0625-inch frame was cemented with rubber cement to one of the 0.0625-inch slabs, and a brass supporting frame reinforced the mold when the uncured rubber was being pressed into it. The thickness of
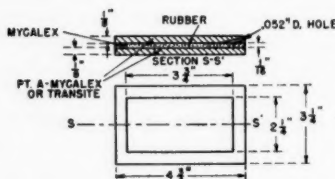
Fig. 3.—Rubber mold for radio-frequency cures.

the brass frame was slightly greater than the mold so as to absorb the high pressure of the hydraulic press when the plates were pressed together during the filling process.

A small hole (No. 55 drill) was drilled diagonally through the upper 0.0625-inch plate to admit a thermocouple hypodermic needle.   The needle itself was 2 inches long and 0.040-inch in diameter; it had two 0.005-inch copper-copnic wires soldered with silver to the needle tip.

The porosity of the Transite was diminished by the application of General Electric silicone lacquer No. 9982 and baking for 4 hours at 300° C.   This prevented the rubber from sticking to the mold and gave a smooth surface to the sample.

Temperature measurements on the high-frequency cured rubber samples were made by inserting the thermocouple needle which was connected to a General Electric photoelectric recorder, an instrument which plots temperature continuously as a function of time.   The temperature on the steam press-cured samples was measured by the needle technique, except that a thermocouple potentiometer was used.   This instrument had been used previously as a standard for calibrating the photoelectric recorder.

The steam-press mold consisted of a 0.0625-inch brass frame with two smooth steel plates on either side.   The brass frame was provided with a hole for inserting the thermocouple needle.   The press itself had 8- by 9-inch plate faces and a 4.125-inch diameter ram.

The composition of the rubber mix was that recommended by the 1935 Rubber Division Committee of the American Chemical Society as follows:

Ingredient	Parts by weight
Pale crepe	100
Zinc oxide	6
Sulfur	3.5
Stearic acid	0.5
Mercaptobenzothiazole	0.5

These are the basic ingredients for a typical pure-gum stock, in the order listed: rubber, filler and activator; vulcanizing agent; acid radical (to furnish a soluble zinc salt); and accelerator.   The ingredients were weighed to an accuracy of ±0.25 per cent and batches of from 500 to 1000 grams were made up at a time.   When not in use, all mixed batches were stored in a refrigerator at 11° C and a relative humidity of approximately 67 per cent.

The milling specifications which were finally adopted were as follows for a 500-gram batch of rubber, using 6-inch diameter rolls, 12 inches wide, with a working distance of 11.5 inches: separation of rolls, 0.060 inch; slow-roll speed, 24 r.p.m. with a 1 to 1.4 ratio; and sufficient cooling water to keep roll temperature around 50° C.   The raw rubber was broken down for 10 minutes and the ingredients were added in this order: mercaptobenzothiazole; stearic acid; zinc oxide; and sulfur.   The batch was cut six times alternately from each side; the cut extended two thirds of the way across the roll and was pulled out until the roll bank disappeared.   The batch was then cut across and ended six times; it was inserted endwise in all cases except the last.   The rolls were then opened up to give a sheet about 0.085-inch thick when cool.   The total milling time was about 20 minutes.

A Scott pendulum-type tester was used for measuring tensile stress and elongations.   Standard dumbbell test-specimens were used.   The die had a

reduced section of 1 by 0.25 inch.   The thickness of the samples varied from 0.062 to 0.075 inch, depending on the particular mold that was used.   All tensile strengths were referred to the unstretched thickness of the sample. Standard grips were used as shown in Figure 5[1].

Elongations were measured by the two-observer method, even though a spark recorder was available on the Scott tester.   One operator held the zero of the rule coincident with an upper gage line on the constricted section of the test strip, while the other operator recorded the tensiles at each 0.5-inch increment of elongation of the lower gage line.   This method enabled the operators to focus their attention on the elongation, and yielded a reproducible stress-strain curve.   The speed of separation of the lower grip was 20 inches per minute.   Samples were always cut with the long dimension in the direction of rolling.

EXPERIMENTAL PROCEDURE

A strip was cut from the uncured rubber stock weighing 9.5 grams.   This was run through the mill twice to freshen up the stock, and then was placed in the mold with the direction of rolling along the long dimension of the mold.

FIG. 4. TYPICAL CURING CYCLES
--- RADIO-FREQUENCY HEATING
— STEAM PRESS HEATING
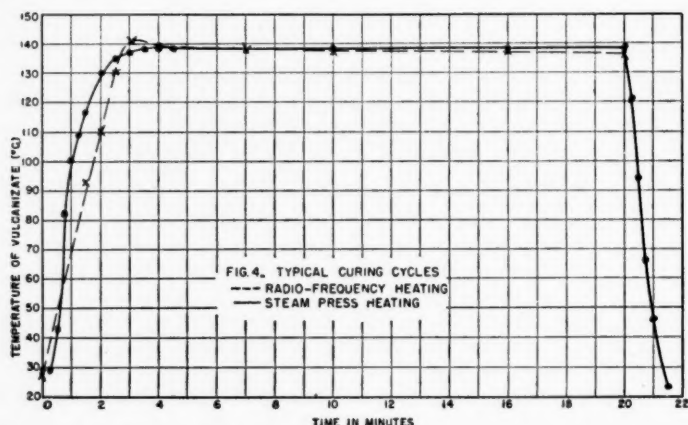
The rubber was warmed up to about 60° to permit easy flowing and the Mycalex (or Transite) plates were pressed together in the frame described under "Apparatus".   The mold was immediately cooled and, after removal from the brass frame, was ready for high-frequency curing.

The solid curves of Figure 4 show the time-temperature relationship for a sample cured in a steam press, starting with a cold press.   Thus, knowing the length of time required to attain temperature equilibrium with the steam cure, the radio-frequency generator field strength could be adjusted by a Variac to give a similar rate of rise and then be cut back to maintain a constant temperature.   A typical electronic curing cycle is shown in Figure 4.

All temperature measurements on the electronic cures were made with the radio-frequency generator shut off except when only a monitoring reading was desired.   This eliminated heating of the needle by eddy currents and also any induced current effects, which would give false temperature readings.   Ex-

perimentally, it was found that the thermal capacity of the needle was sufficiently small, in comparison to that of the rubber, to allow the needle, at room temperature, to be inserted into the hot rubber and a temperature measurement to be made before cooling began. This entire operation required about 5 to 10 seconds. That this was a true indication of the temperature was verified by plotting the cooling curve on a semilog scale and extrapolating back to zero time. One unsuspected source of error was heating of the needle by friction when it was quickly pulled in or out of the sample. This amounted to 5° or 10° and could be minimized by moving the needle slowly in or out of the sample. While the sample was being cured electronically, during which time the electric field was relatively small, the thermocouple needle could be left in the rubber without any arcing. Under these conditions the temperature reading was high by about 10°, but the reading remained constant for a given field strength and needle position so that under controlled conditions the constancy of temperature could be monitored. With this technique, the temperature could be held within about a 3° spread, excluding any initial overshoots which amounted in the worst cases to 10° for approximately 3 minutes out of 60. Tests showed that these variations were not discernible in the tensile stress measurements.

At the end of a curing period by radio frequency, the sample was quickly removed from the electrodes and placed on a copper slab in the freezing compartment of a refrigerator. It required approximately 3 minutes to reach room temperature, which is comparable to the 2 minutes required for the press samples to cool.

All samples were stored in a refrigerator approximately 24 hours after curing before tensile measurements were made. A check run on this stock showed that over an 8-day storage period the tensile strength rose only 8 per cent, substantially all of which had occurred after 24 hours. Therefore, a 24-hour period seemed a practical choice for allowing the cured samples to come to equilibrium.

EXPERIMENTAL ERRORS

Temperature.—The variation for the steam cured samples was ±0.5° C of the indicated temperatures. The corresponding variation for radio-frequency cured samples was ±1.5° C, excluding fluctuations at the beginning of a run which were of negligible time duration.

Tensile strengths.—Because the ultimate tensile strength (occurring at break) of a rubber sample is a test to destruction, there are a number of influencing variables which may or may not be controllable; these lead to well known erratic results for such measurements. In general, the measured tensile strengths of dumbbell samples having the same cure will be shown on graphs as points with a vertical line extending ±5 per cent above and below the average value. Usually, this normal 10 per cent spread included all the test points, but occasionally the spread was closer to 20 per cent. The tensile stresses at various stages of elongation are probably more reproducible figures than the ultimate tensile strengths. Some test-specimens, which were badly under- or overcured, did not break at the constricted portion of the sample. The observed tensile strengths for these improper breaks must be considered low, and are indicated by an arrow pointing upward.

Curing times were known to be better than ±0.5 minute. In view of the relative insensitivity of tensile strength to this brief period, it was the most accurately known independent variable.
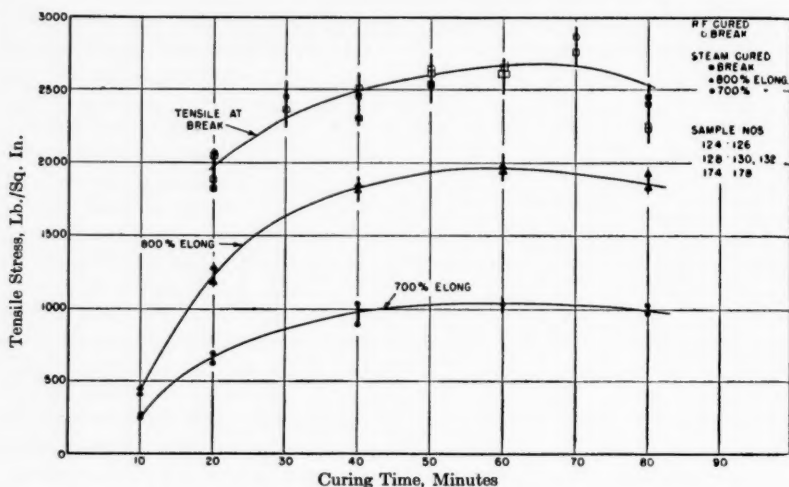
Fig. 5.—Tensile stress *vs.* curing time.
Mycalex plates on radio-frequency mold; radio-frequency curing temperature, 139.5° C:
steam curing temperature, 137.1° C: batch 11.

DISCUSSION OF RESULTS

Tensile stress as function of time.—In accordance with the usual determination of the optimum cure (cure giving maximum tensile strength as observed at break) of a given rubber compound, a series of step-cures with a fixed steam pressure (temperature) were made with different lengths of curing time. In Figure 5, the observed tensile stresses are plotted against the curing time for 700 and 800 per cent, and ultimate elongation. The radio-frequency curing temperature was 135.5° C, and the results obtained for these samples are ultimate tensile values only. Measurements on samples cured by steam were made at a temperature of 137.1° C. Within the limits of experimental error, the tensile stresses of the samples cured by the two methods are in agreement.
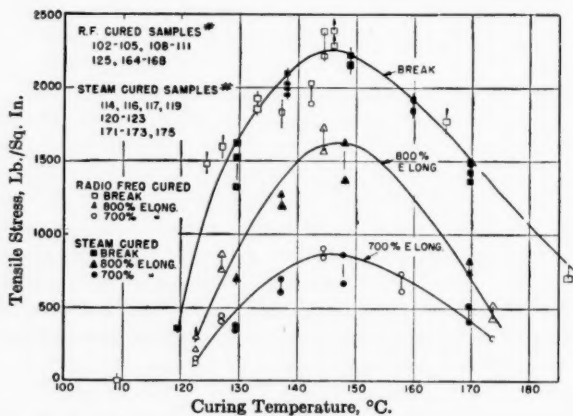
Fig. 6.—Tensile stress *vs.* curing temperature.
Mycalex plates on radio-frequency mold; 20-minute curing time; batch 11.

This type of plot also demonstrates the insensitivity of tensile stress to time; hence, it is not particularly suited to bring out possible differences between the two methods of heating. The highest tensile of 2650 lbs. per sq. in. occurs for about 1 hour cure at 137° C. Ultimate tensile strengths of 2800 lbs. per sq. in. were obtained on this same stock after standing for 8 days.

Tensile stress as function of curing temperature.—In this series of runs, the independent variable was taken as the tempersture and the curing time was held constant. Figure 6 shows the results when the curing time was 20 minutes and the observed tensile strengths at break and 700 and 800 per cent elongations. Within experimental error the steam cures coincide well with the electronic cures. Because it was difficult experimentally to make the initial rates of temperature rise exactly the same in the two methods of curing, this difference was minimized by increasing the curing time from 20 to 60 minutes and repeating the run; the results were the same, as shown in Figure 7. These
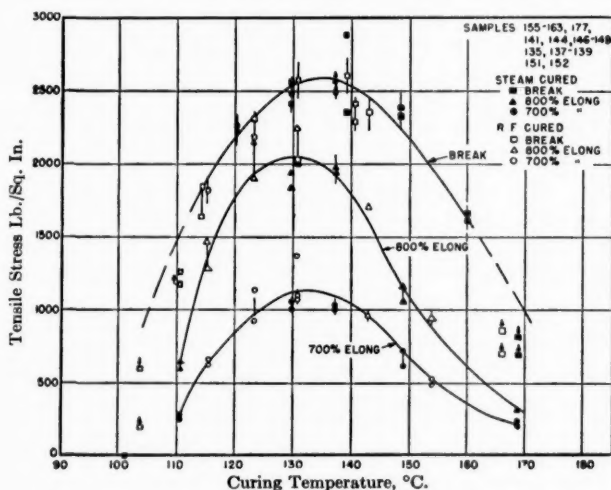
FIG. 7.—Tensile stress *vs.* curing temperature.
Mycalex plates on radio-frequency mold; 60-minute curing time; batch 11.

curves are consistent with those of Figure 5 in that the optimum cure occurs at 135° C for 60 minutes curing time. Tripling the time of cure corresponds to a temperature change from 146° to 135° C to obtain optimum properties. This falls roughly in line with the usual rule of thumb regarding ordinary chemical reactions, in that the reaction rate is doubled by a 10° rise in temperoture. The values of tensile stress for the radio-frequency cured samples are the same as for the steam press cured ones; there was no difference in the quality of the vulcanizate obtained as determined by tensile stress.

In three runs the part, *A*, of Figure 3, which constitutes the bulk of the rubber mold used for radio-frequency cures, was made of Mycalex. The choice of this material was made for the following reasons. The loss factor is only about one-fourth that of the rubber compound; it has high heat resistance; it is mechanically strong, and does not soften in this temperature range; it machines fairly well; it has low thermal conductivity; and it is readily available in standard stock sizes. With a mold of this type the chief source of heat,

as a result of dielectric losses, is the rubber itself and, even with an abundance of thermal insulation, there necessarily exists a considerable temperature gradient across the rubber slab. This gradient was most pronounced in the early stages of heating and with thick samples actually resulted in an over-curing of the center of the rubber with less curing at the surfaces. Color changes on a 0.125-inch thick slab of rubber demonstrated this to be the case. However, by reducing the thickness to 0.0625-inch, this temperature gradient in the rubber was sufficiently minimized so that the color change was no longer visible to the eye. To create a gradient in temperature which was the inverse of the above, a duplicate run with Transite plates as the part, A, of Figure 3 was carried out. Transite is very hygroscopic, and dielectric losses vary considerably, depending on the dryness. It was estimated that the material used in this investigation showed losses about twenty times greater than the rubber. Therefore, with a Transite mold, there is a closer simulation of the conditions which exist in a steam press cure when the rubber is heated at its
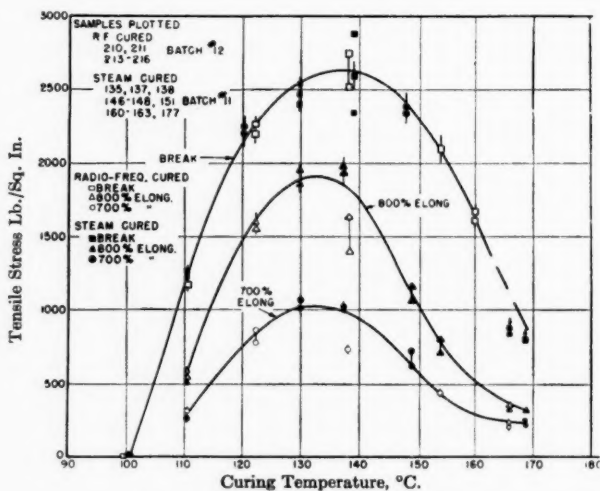
FIG. 8.—Tensile stress *vs.* curing temperature.
Transite plates on radio-frequency mold; 60-minute curing time.

surface by the adjacent press plates. In Figure 8 there are plotted the tensile stresses observed on samples cured on the Transite mold for 60 minutes. The radio-frequency and press cured samples show the same tensile stress-temperature dependence over the entire curing range.

Figures 6, 7, and 8 show that, regardless of the method of heating, the same mechanical properties are obtained for a given time and temperature of curing.

Combined sulfur.—Samples were selected from the runs graphed in Figures 5 and 6 and analyzed for combined sulfur. As used here, combined sulfur is the sulfur which has gone into chemical combination with rubber molecules during the curing process. By calculation there is a theoretical maximum of 3.16 per cent by weight of sulfur which is available for chemical combination. In Figures 9 and 10 the combined sulfur is plotted as a function of curing time and curing temperature, respectively. The radio-frequency cured and press-cured samples again exhibit the same behavior which is completely consistent

FIG 9
CURING TEMP VS % COMBINED SULPHUR
CURING TIME = 20 MIN
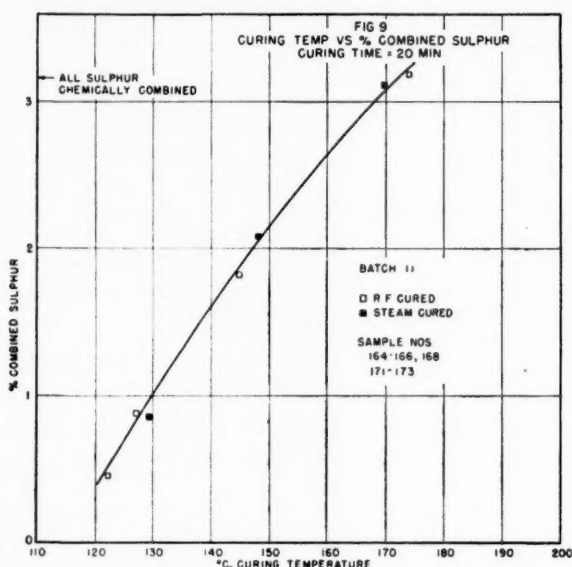
with the tensile-stress measurements. In the ranges of time and temperature covered, nearly all the sulfur has united with the rubber. Thus, it may be concluded that the same thing happens chemically whether rubber is cured by dielectric losses or by the more conventional steam press heating.

Dielectric behavior.—In Figure 11 there are plotted the dielectric constant (ϵ') and loss factor (ϵ'') dispersion curves for samples cured for 80 minutes at 137° C—one in a steam press and the other by radio-frequency. Both samples show nearly identical behavior with an absorption peak at 6.0 megacycles. The differences in magnitude of the loss factor maximum may be due to differences in amounts of combined sulfur caused by slight differences in cure. The vulcanizate has only a small amount of electrolyte conduction as evidenced by the low values of ϵ'' in the low frequency region. The absorption maxima,

FIG 10
CURING TIME VS % COMBINED SULPHUR

249 - STEAM CURED

256 - R.F CURED

DIELECTRIC LOSS FACTOR VS LOG FREQUENCY

FIG 11 RUBBER SAMPLES CURED FOR 80 MIN AT 137°C.
BATCH 9 - STANDARD MIX
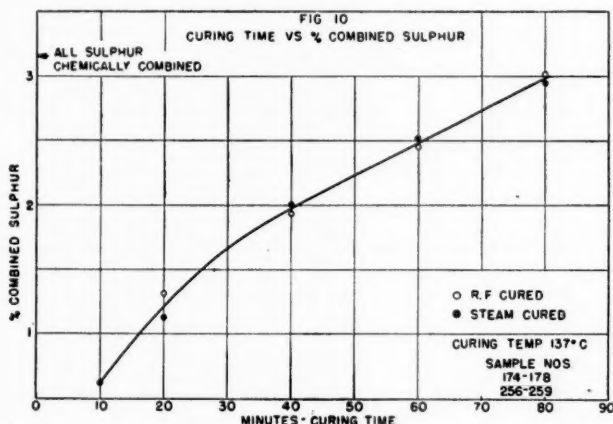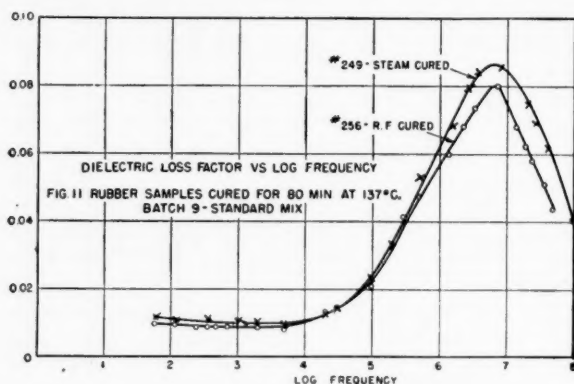
LOG FREQUENCY

which are very likely caused by polar groups introduced by vulcanization with sulfur, occur at the same frequency; hence, the end products are the same regardless of the method of curing.

Effect of voltages on curing rate.—To ascertain whether there was any possible effect of voltage on the rate of radio-frequency curing, some samples were cured by applying a constant radio-frequency voltage of 0.75 kv. per cm. for varying periods of time. A record of the temperature was made for the entire curing cycle, including both heating and cooling. The radio-frequency was shut down momentarily to read the temperature at 1-minute intervals during the heating part of the cycle, and the hot mold was placed between the two cold copper blocks for rapid cooling after the rubber had reached the desired temperature. With this technique the radio-frequency curing cycle was comparable to that obtained when the rubber mold plus 0.125-inch sheets of Transite were placed in a steam press whose plates were maintained at 180° C.

For each sample cured, a plot of an arbitrary curing intensity function[2], assumed to be $I = 2^{T/10}$ (T in ° C) was made against time. The area under this curve, which is the integral $\int_0^t 2^{T/10} dt$, was measured by a planimeter, and these values were plotted against the measured tensile stress. Such a plot takes into

STEAM CURED SAMPLES
217-220
222-226

R.F. CURED SAMPLES
238, 241, 242, 244, 245

FIG. 12
ULTIMATE TENSILE STRENGTH VS THERMAL CURE FACTOR ($\int_0^t 2^{T/10} dt$)

□ - R.F. CURED, FIELD STRENGTH=¾ KV/CM

■ - STEAM CURES

TRANSITE MOLD

APPROX. MINUTES CURE

$\int_0^t 2^{T/10} dt$
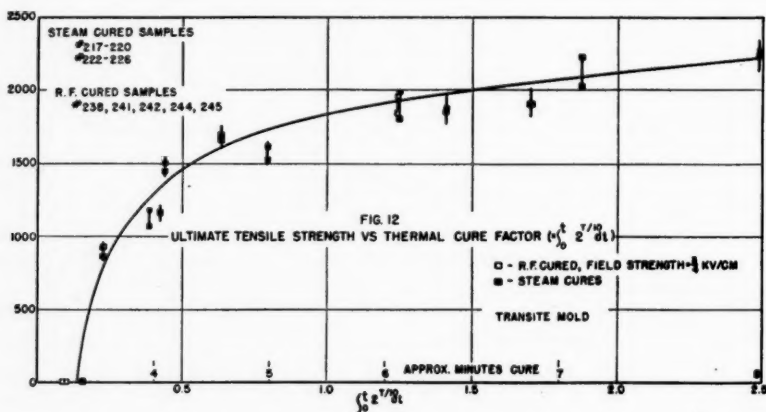
account the variation of temperature as well as time which necessarily occurs when the field strength of the radio-frequency generator is held constant throughout the cure.

In Figure 12 there is plotted the tensile stress at break against the thermal cure factor ($\int_0^t 2^{T/10}dt$). The scale of the latter variables is in arbitrary units. The radio-frequency cured samples coincide, within experimental error, with the steam-cured samples, under the conditions of measurement here. The tensile stress gradually increased throughout the range of cures that were covered. On the basis of the complete tensile data given in Figure 8, the optimum cure would be expected to occur for a thermal cure factor value of 3.7; this checks qualitatively with Figure 12. Because of the exponential depend-ence of cure factor on temperature, the optimum cure is reached in a very short time compared to the customary cures at lower temperatures. From these data, it was concluded that there is no large voltage effect on the rate of curing over the initial part of a series of step-cured samples. To determine more precisely any small differences in rates of curing between the two methods of heating, it would be necessary to extend the range of cures to include the opti-mum and overcured samples.

ACKNOWLEDGMENT

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RECLAIMING AGENTS FOR
SYNTHETIC RUBBER *

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With the advent of synthetic rubbers during the recent war emergency, the problem of reclaiming these new products became of vital interest to the reclaimer. After preliminary experiments were undertaken, it became evident that methods and materials used for manufacturing natural rubber reclaim would not be immediately applicable for reclaiming synthetic rubbers. It was therefore necessary to develop new procedures, plasticizers, and chemicals in order that synthetic reclaim should be practical when the supply of natural rubber scrap disappeared. Since the major portion of the production of synthetic rubbers was to be of the butadiene-styrene type—that is, GR-S— active research was undertaken to develop suitable means for reclaiming vulcanizate scrap obtained from this polymer.

The first laboratory tests on reclaiming GR-S, using methods applied to natural rubber, resulted in a dry, hard, and brittle product which could scarcely be considered reclaimed rubber. Further work indicated that large amounts of oil plasticizers and tackifiers were necessary to prepare a product possessing workability properties similar to natural rubber reclaim. Even with such large amounts of oils and tackifiers the quality of the reclaim was poor. This product had a low hydrocarbon content and a high acetone extract because of the added oils. The problem then facing the reclaimer was the discovery of new and more active reclaiming agents or peptizers for GR-S scrap.

A *reclaiming agent,* as the term is used in the present work, may be defined as a chemical which acts as a catalyst in hastening the process of reclaiming vulcanized natural or synthetic rubber scrap. These reclaiming agents should be distinguished from the oils and resins which are used as swelling agents, plasticizers, and tackifiers in the various reclaiming processes. As catalysts or promoters, the reclaiming agents are most often employed together with the usual plasticizers and tackifiers. The effective reclaiming agents are required in much smaller quantities than the usual swelling oils and tack-producing resins.

The use of organic chemicals as catalysts for the reclaiming processes for natural rubber began as early as 1910 when Lutz[1] described the use of aniline. More recently, the use of the reaction products of monoarylhydrazines with aldehydes and ketones has been reported[2]. The aromatic thiols as reclaiming agents for natural rubber have been covered by Garvey[3], Neal and Schaffer[4], and Gumlich and Ecker[5]. Dasher used various hydroxylamines, aliphatic amines, aliphatic polyamines, and their mercapto derivatives.[6]

As the result of wartime activity in the reclaiming of synthetic rubber in general and of GR-S in particular, the use of both long-chain aliphatic amines and cyclohexylamine[7] has been reported. The aromatic thiols, as covered in

the Garvey patent[3], also were found to have some activity in GR-S[7].   These reclaiming agents, however, were later superseded by the more active cresol–sulfur chloride reaction products of Kirby and Steinle[8].

The use of aromatic thiols for reclaiming various types of synthetic rubber scraps or vulcanizates has had a parallel development in England[9] and Germany[10].   The English materials are known as the RRA's and the German materials were sold under the name of Renacit.   The chemical compositions of Renacit I, II, and III were, respectively, β-thionaphthiol, trichlorothiophenol, and 9-thioanthrol.   Each succeeding material was reported to have possessed a reduced irritating effect on the skin with approximately equivalent activity as a reclaiming agent for Buna-S.

As a result of a large number of tests carried out in this laboratory during the past several years, it has been found that the sulfides prepared from certain highly alkylated phenols are extremely active catalysts for reclaiming GR-S and other synthetic rubbers.   The object of this paper is to report the preparation, evaluation, and structural correlation of these new materials with respect to their activity as reclaiming agents.

PREPARATION OF RECLAIMING AGENTS

The phenol sulfides used in this investigation were prepared in a three-necked flask fitted with a reflux condenser, a mercury seal stirrer with electric motor drive, and a dropping funnel.   The reactions were carried out at the boiling points of the solvents used, either carbon tetrachloride or ethylene dichloride, and heat was applied by an electric heating mantle controlled by a variable voltage transformer.

In all cases, except where otherwise indicated, the ratio of 2 moles of alkylphenol to 1 mole of sulfur monochloride was used in the sulfide preparations. After the addition of the sulfur monochloride was complete, the mixture was allowed to stir for half an hour and the solvent was then distilled in vacuo, care being taken to remove the last traces without overheating the product.

The crude mixture of sulfides of the alkylphenol formed by the above procedure was used without further purification unless otherwise indicated.   In the following paragraphs this reaction mixture is referred to as the alkylphenol sulfide.   Many of these sulfides have not been recorded in the literature, and it is expected that some of them will constitute a communication from this laboratory in the near future.

RECLAIMING PROCEDURE

A pan heater or open steam type reclaim, made from 100 per cent GR-S vulcanized tread stock, was chosen to compare the various reclaiming agents to be tested.   The vulcanized stock was obtained by securing a factory lot of 100 per cent GR-S tread compounds, curing in open steam, and then grinding to pass a 5-mesh screen.   No natural rubber contamination was permitted in the preparation of this scrap.

A reclaiming recipe for this scrap was developed which contained the following ingredients:

GR-S tread scrap (5-mesh)	200 parts
Dipentene fraction[a] (b.p. 173° to 201° C)	12 parts
Coumarone indene resin[b]	12 parts
Reclaiming agent	3 parts

[a] Solvenol, supplied by Hercules Powder Company.
[b] Cumar 2½ MH, supplied by Barrett Division, Allied Chemical & Dye Corporation.

The swelling agent, tackifier, and reclaiming agent were weighed out, heated together gently until solution was obtained, and then incorporated into the scrap by use of a laboratory Baker-Perkins mixer. After mixing, the scraps were aged for at least 6 hours before the reclaiming operation. The heating process was carried out in a laboratory pan heater; the scrap was subjected to open steam of 175 pounds per square inch for 4 hours. After completion of the heating period, factory vacuum was applied to the stock in the heater for a period of 1 hour to ensure dryness. The softened scrap mass in biscuit form was then removed from the heater and allowed to cool to room temperature. Up to fifteen or more individual reclaims could be made in one cooking period.

The softened biscuit from the heating operation was removed from the pan, blended, and massed by four passes through an open laboratory mill, to ensure uniformity. Approximately 50-gram portions of each biscuit in a group of reclaims were then refined three passes on a cool (110° F) laboratory mill. This mill was equipped with a refiner knife and was tightened to the proper setting, so that a thickness of 0.005 inch was obtained when a piece of lead or solder was passed between the rolls. Each group of reclaims was refined in consecutive series, each pass through the mill, in order that each reclaim sample in the group might receive the same refining treatment.

EVALUATION OF RECLAIM SHEET

The evaluation of a reclaim sheet has been a problem peculiar to the reclaimer. This evaluation has been largely an art, based on the manual observation of the individual technician. In this laboratory three essential properties have been observed and recorded in the evaluation of a refined reclaim: sheet thickness, body, and tackiness, the last two properties being estimated by hand evaluation. The overall hand evaluation is often referred to in the industry as the workability of the reclaim.

In addition to the above properties, it has been shown during the course of the present work that valuable quantitative data may be obtained on the refined reclaim by the use of the Mooney plastometer[11] and also by the determination of the tensile strength and elongation of the refined sheet. In the latter case a 0.25-inch restricted area dumbbell was died out from the three-pass refined reclaim sheet and pulled on a small Scott tensile machine (Model X-5), with a range of 2 pounds at a rate of 20 inches per minute. The data so obtained agree qualitatively with the previously used evaluation tests of thickness, body, and tackiness and with the overall hand evaluation or workability of the reclaim. These types of data, as exemplified by thickness, plasticity, and tensile properties of the uncured, refined reclaim sheet, tend to tie down the differences between reclaims to measurable quantitative amounts. However, these methods have not been used long enough to establish completely their validity in commercial practice.

The thickness of the reclaim sheet was measured, immediately after refining, with a Randall-Stickney thickness gage. Measurements were made across the entire sheet at a point approximately 5 inches from the end of the sheet as it was cut from the roll by the refiner knife. The average value of sheet thickness, in inches, was considered to be a measure of the softness of the reclaim, and consequently of the activity of the reclaiming agent.

The body rating of the sheet was estimated by observing the stretch or elongation of the refined sheet, stretched by hand, and by the appearance and

uniformity of this stretched sheet. The body was rated as very good (V-G), good (G), fair (F), poor (P), very poor (V-P), tough (T), and lacy (L), or as some combination of these. A good sheet must have satisfactory elongation without tearing, and a smooth uniform appearance. A poor sheet has poor stretch or elongation, tears, and may be nonuniform, tough, and lacy.

In a number of cases these normal body evaluations have been given numerical ratings as follows:

V-G	Very good	6
G	Good	5
G⁻	Good	5⁻
F⁺	Fair	4½
F	Fair	4
P-F	Poor-fair	3½
P-F⁻	Poor-fair	3
P-L	Poor-lacy	2
P	Poor	1
V-P-L	Very poor-lacy	½
V-P-T	Very poor-tough	½

These numerical ratings facilitate the formation of a quality index by addition of the tackiness ratings (below), which should be approximately equivalent to the overall workability of the reclaim as referred to in the reclaiming industry.

The third property of the refined reclaim sheet was that of tackiness—defined as the tendency of the refined reclaim sheet to adhere to itself. It was estimated by laying a portion of the refined reclaim sheet across the hand and then pressing the thumb and the first finger of the hand together. When the thumb and first finger were spread apart, a small but definite force was required to separate the two adhering surfaces. A rating of 5 was given to the force required to separate a sheet of typical natural rubber whole tire reclaim. Milled crude rubber was given a rating of 10 and crude GR-S with no tackiness was given a rating of zero. This is essentially the same method and the same scale used previously[12] in this laboratory for the estimation of the tackiness in milled sheets of unvulcanized GR-S with and without added tackiness-producing compounds. Values between those assigned to the controls mentioned above were estimated by the observer and could be duplicated easily by different independent observers with an accuracy of ±1 unit.

ALIPHATIC AND AROMATIC THIOLS AS RECLAIMING AGENTS

A comparison of the aliphatic and aromatic thiols as reclaiming agents was made desirable by the activity reported for certain aromatic thiols[7]. The controls contained 4,6-di-*tert*-butyl-3-methylphenol sulfide, the reaction product of 4,6-di-*tert*-butyl-3-methylphenol and sulfur monochloride.

The first part of the data in Table I covers the aromatic thiols. Thiophenol as the first member of this series was found to be somewhat more active than phenol, its oxygen counterpart. The isomeric thiocresols showed no advantages over thiophenol, but the thionaphthols were somewhat more active. Compounds containing the naphthalene nucleus were usually slightly more active than the corresponding benzene compounds.

The aliphatic thiols were very poor reclaiming agents in this process, and much less active than the aromatic thiols. It was apparent that the variation in the chain lengths of the aliphatic compounds had very little effect on their activity in this process.

TABLE I

THIOLS

Compound	Thickness	Body	Tackiness	Quality index	Mooney value, MS/4/212
Control (4,6-di-*tert*-butyl-3-methylphenol sulfide)	0.008	G⁻ (5)	4⁺	9	41
Phenol	0.020	P-L (2)	1	3	69
Thiophenol	0.013	P-F⁻ (3)	2⁺	5½	56
o-Thiocresol	0.012	P-F (3½)	2⁺	6	52
m-Thiocresol	0.013	P-F (3½)	2⁺	6	54
p-Thiocresol	0.011	P-F (3½)	2⁺	6	52
α-Thionaphthol	0.010	F (4)	4⁻	8	47
β-Thionaphthol	0.010	F (4)	3	7	52
Octanethiol	0.025	P-L (2)	1⁺	3½	70
Decanethiol	0.020	P-L (2)	1⁺	3½	66
Dodecanethiol	0.020	P-L (2)	1⁺	3½	68
Tetradecanethiol	0.025	P-L (2)	1⁺	3½	67
Hexdecanethiol	0.020	P-L (2)	1⁺	3½	64

ALKYL PHENOL SULFIDES AS RECLAIMING AGENTS

The reclaims made from the alkylphenol sulfides were compared in groups in vulcanized GR-S scrap, as shown in Table II. Each group included a reclaim sample containing the 4,6-di-*tert*-butyl-3-methylphenol sulfide as a control. This remained fairly constant throughout the study. The Mooney plasticity values of the control varied from 34 to 41 (average 36.5) in ten different runs. The relative ratings for body and tackiness of the reclaim sheet also remained the same, within reasonable limits, in these runs.

Only minor differences were observed between the several isomeric cresol sulfides and between the several isomeric xylenol sulfides. The xylenol sulfides were of slightly higher activity than the cresol sulfides, as indicated by the Mooney plasticity values, while the unsymmetrically substituted trimethylphenol sulfide was much more active than either.

The *p-tert*-amylphenol sulfide showed approximately the same activity as the reaction product of phenol and sulfur monochloride. However, a large increase in activity was observed between the *p*-amyl- and the 2,4-diamylphenol sulfides. The 2,4,6-triamylphenol sulfide dropped off considerably in activity. The cyclohexanol–sulfur monochloride reaction products prepared from the unsubstituted, the monoamyl, and the diamylcyclohexanols all were somewhat less active than the corresponding benzene derivatives. The diamylcyclohexanol sulfide was fairly close in activity to 2,4-diamylphenol sulfide.

A series of mono-*p*-alkyl substituted phenol sulfides with alkyl groups containing one to nine carbon atoms, produced reclaims uniformly poor in quality, which made it difficult to report any significant differences in their properties. Variations in chain length in the *p*-alkyl group made little difference in the activity of the reclaiming agents.

The unsubstituted and the butylated cresols were compared. The sulfide prepared from 2-butyl-4-methylphenol was much more active than that prepared from *p*-cresol. The most active sulfide in this series was that prepared from 4,6-di-*tert*-butyl-3-methylphenol. The 2,4,6-substituted compounds closely related to the latter compound—that is, the sulfides prepared from 2,4-dimethyl-6-butylphenol and 2,6-di-*tert*-butyl-4-methylphenol—were found to be very low in activity.

TABLE II

ALKYL PHENOL SULFIDES AS RECLAIMING AGENTS

Compound	Thickness	Body	Tacki-ness	Quality index	Mooney value, MS/4/212
Methyl and dimethyl phenol sulfides					
Control	0.012	G (5)	5	10	35
Phenol $+ S_2Cl_2$	0.020	P (1)	1+	2½	54
o-Cresol $+ S_2Cl_2$	0.015	P-F (3½)	2+	6	53
m-Cresol $+ S_2Cl_2$	0.020	P-F (3½)	2	5	48
p-Cresol $+ S_2Cl_2$	0.020	P (1)	1+	2½	59
3,5-Dimethylphenol $+ S_2Cl_2$	0.015	F+ (4½)	3+	8	45
2,4-Dimethylphenol $+ S_2Cl_2$	0.015	F-G (4½)	4	8½	46
3,4-Dimethylphenol $+ S_2Cl_2$	0.015	F-G (4½)	4-	8	48
2,5-Dimethylphenol $+ S_2Cl_2$	0.015	F+ (4½)	4-	8	
Methyl, ethyl, and trimethyl phenol sulfides					
Control	0.005	G+ (5½)	6+	12	36
Phenol $+ S_2Cl_2$	0.008½	P (1)	2+	3½	58
m-Cresol $+ S_2Cl_2$	0.009½	P (1)	2+	3½	53
m-Ethylphenol $+ S_2Cl_2$	0.011	P+-T (1½)	3+	5	52
p-Ethylphenol $+ S_2Cl_2$	0.010	P-L (2)	2+	4½	59
3-Methyl-5-ethylphenol $+ S_2Cl_2$	0.008½	F (4)	3+-4-	7½	51
3,5-Dimethylphenol $+ S_2Cl_2$	0.008½	F- (3½)	3+-4-	7	49
2,3,5-Trimethylphenol $+ S_2Cl_2$	0.004½	G- (4½)	6+	11	36
Amyl, diamyl, and triamyl phenol sulfides					
Control	0.007	G (5)	5+	10½	38
Phenol $+ S_2Cl_2$	0.018	P (1)	1+	2½	61
p-tert-Amylphenol $+ S_2Cl_2$	0.020	P (1)	1+	2½	63
2,4-Di-tert-amylphenol $+ S_2Cl_2$	0.010	F- (3½)	4	7½	44
2,4,6-Tri-sec-amylphenol $+ S_2Cl_2$	0.014	P-F (3½)	2	5½	47
2,4-Di-sec-amylphenol $+ S_2Cl_2$	0.010	F (7)	4-	7½	59
Amyl and diamyl cyclohexanol sulfides					
Control	0.006½	G (5)	6-	10½	40
Phenol $+ S_2Cl_2$	0.011	P (3)	2	3	66
Cyclohexanol $+ S_2Cl_2$	0.014	P-T (1)	2-	2½	84
p-tert-Amylphenol $+ S_2Cl_2$	0.012½	P-F-T (3½)	4-	7	64
p-tert-Amylcyclohexanol $+ S_2Cl_2$	0.015½	P-T (1)	2	3	75
2,4-Di-tert-amylphenol $+ S_2Cl_2$	0.009	F- (3½)	5	8½	45
Diamylcyclohexanol $+ S_2Cl_2$	0.009	F- (3½)	4+	8	50
p-Monoalkyl phenol sulfides					
Control	0.006½	G (5)	6-	10½	40
Phenol $+ S_2Cl_2$	0.011	P (1)	2	3	66
p-Cresol $+ S_2Cl_2$	0.0112	P-F-T (3½)	3+	6½	66
p-Ethylphenol $+ S_2Cl_2$	0.011	P-L (1)	3-	3½	64
p-tert-Butylphenol $+ S_2Cl_2$	0.012	P-L (1)	4-	4½	67
p-tert-Amylphenol $+ S_2Cl_2$	0.012½	P+-F-T (3½)	4-	7	64
p-Hexylphenol $+ S_2Cl_2$	0.011	P+-F (3½)	3	6½	64
p-Octylphenol $+ S_2Cl_2$	0.011	P-L (2)	4-	5½	61
p-Nonylphenol $+ S_2Cl_2$	0.012	P-L (2)	2+	4½	60
Butyl and dibutyl methyl phenol sulfides					
Control	0.004½	G (5)	6	11	37
Phenol $+ S_2Cl_2$	0.010	P-L (2)	2-	3½	58
p-Cresol $+ S_2Cl_2$	0.0082	P-L (2)	1-	3½	56
4-tert-Butyl-3-methylphenol $+ S_2Cl_2$	0.005½	F+ (4½)	5	9½	45
2-Butyl-4-methylphenol $+ S_2Cl_2$	0.005	F+ (4½)	5-	10	43
2,4-Dimethyl-6-butylphenol $+ S_2Cl_2$	0.010	P-L (2)	1	3	59
2,6-Di-tert-butyl-4-methylphenol $+ S_2Cl_2$	0.008½	P-L (2)	2-	5½	59
4,6-Di-tert-butyl-3-methylphenol $+ S_2Cl_2$	0.004½	G (5)	6	11	37
Variation of alkyl phenol–sulfur monochloride ratio					
Control	0.003½	P (1)	7+	7½	33
Phenol $+ S_2Cl_2$	0.010½	P-L (2)	2-	4½	54
4-tert-Butyl-3-methylphenol	0.010	P-L (2)	1-	3½	57
4-tert-Butyl-3-methylphenol $+ S_2Cl_2$ (1.0–0.50)	0.005½	F+ (4½)	5	9½	41
4-tert-Butyl-3-methylphenol $+ S_2Cl_2$ (1.0–0.75)	0.005	F+ (4½)	6	9½	40
4-tert-Butyl-3-methylphenol $+ S_2Cl_2$ (1.0–1.0)	0.005	F+ (4½)	5-	9½	41
4-tert-Butyl-3-methylphenol $+ S_2Cl_2$ (1.0–1.25)	0.007	F- (3½)	3-	6½	46
Sulfide, sulfoxide, sulfone, and sulfur chloride reaction products					
Control	0.005½	G (5)	6	11	32
Phenol $+ S_2Cl_2$	0.010	VP-L (½)	2-	3½	54
4-tert-Butyl-3-methylphenol sulfoxide	0.010½	F- (3½)	4-	7	45
4-tert-Butyl-3-methylphenol sulfone	0.013½	P (1)	2	3	59
4-tert-Butyl-3-methylphenol monosulfide	0.011	F- (3½)	3	6½	46
4-tert-Butyl-3-methylphenol $+ S_2Cl_2$	0.007½	F (4)	5	9	39
4-tert-Butyl-3-methylphenol $+ SCl_2$	0.009½	F- (3½)	4-	8	43

TABLE II.—*Continued*

Compound	Thickness	Body	Tackiness	Quality index	Mooney value, MS/4/212
Miscellaneous phenol sulfides					
Control	0.004	G⁻ (5½)	6	11½	36
Koppers coal-tar cresylic acid SD[a] + S₂Cl₂	0.008	P (1)	2	3	56
Koppers coal-tar cresylic acid 1-B[b] + S₂Cl₂	0.008½	F⁻-P⁻ (3½)	4⁻	7	53
Koppers coal-tar cresylic acidX-1[c] + S₂Cl₂	0.007	F (4)	4⁺	8½	50
Koppers coal-tar cresylic acidX-2[d] + S₂Cl₂	0.008	F⁻ (3½)	3⁺	7	48
Koppers coal-tar cresylic acid No. 2[e] + S₂Cl₂	0.007	F⁻ (3½)	3⁺	6½	50
Shell petroleum cresylic acid 2000[f] + S₂Cl₂	0.007	F⁻ (3½)	3⁺	6½	48
Shell petroleum cresylic acid 4020 A[g] + S₂Cl₂	0.005½	F-G⁻ (4½)	5⁻-5	9½	42
Shell petroleum cresylic acid 9035 A[h] + S₂Cl₂	0.006½	F⁻ (3½)	4⁻	7	48
Oronite petroleum cresylic acid FF[i] + S₂Cl₂	0.005½	F-G (4½)	5⁻-5	9	42
Oronite petroleum cresylic acid H[j] + S₂Cl₂	0.005½	F-G (4½)	5⁻	9	45
Phenol + S₂Cl₂	0.007½	P (1)	2	3	57
4,4′-Dihydroxydiphenyl sulfide	0.010	P-L (2)	1⁺	3½	66
4,4′-Dihydroxydiphenyl sulfone	0.017	P-L (2)	1⁺	3½	68
Control	0.003½	G (5)	7⁻	11½	33
Phenol + S₂Cl₂	0.010	P-L (2)	2⁺	4½	54
p-Phenylphenol + S₂Cl₂	0.011½	P-T (1)	2	3	57
p-Cyclohexylphenol + S₂Cl₂	0.010	P-L (2)	2	4	56
p-Hexylphenol + S₂Cl₂	0.008½	P-F⁻ (3)	3⁺	6	57
m-Cresol + S₂Cl₂	0.007½	P-F⁻ (3)	2⁺	5	56
Distilled Cardolite 5679[k] + S₂Cl₂	0.010	P-L (2)	2⁺	4½	52
Shell Dutrex 55[l] + S₂Cl₂	0.007½	P-F⁻ (3)	3⁺	6	47
Octyl petroleum cresylic acid 2000[m] + S₂Cl₂	0.007	P-F⁻ (3)	3⁺-4	6	44
Shell petroleum cresylic acid 4020A[g] + S₂Cl₂	0.004½	F (4)	5	9	43
Phenol + S₂Cl₂	0.008½	P (1)	2⁺	3½	58
o- and *p*-Mixed benzylphenols + S₂Cl₂	0.011	P-L (2)	1	3	57
Dibenzylphenol + S₂Cl₂	0.010½	P (1)	2	3	52
Polyhydric phenol sulfides					
Control	0.004½	G (5)	6	11	37
Phenol + S₂Cl₂	0.010	P-L (2)	2⁻	3½	58
Catechol + S₂Cl₂	0.013½	VP-T (½)	1⁻	1	78
Resorcinol + S₂Cl₂	0.015	VP-T (½)	1	1½	91
Hydroquinone + S₂Cl₂	0.013	P-T (1)	1	1½	78
Pyrogallol + S₂Cl₂	0.009½	P-L (2)	1⁺	3½	67
Phloroglucinol + S₂Cl₂	0.011½	P-L (2)	1⁺	3½	78
4-*tert*-Butylcatechol + S₂Cl₂	0.009	P-L (2)	2⁺	4½	77
Di-*tert*-butylcatechol + S₂Cl₂	0.010	P-L (2)	1⁺	3½	75
2,5-Di-*tert*-butylhydroquinone + S₂Cl₂	0.009	VP-L (1½)	1⁺	2	75
Octylcatechol + S₂Cl₂	0.012	VP-L (½)	1	1½	74

[a] Distillation, 50% not above 206° C, dry below 225° C.
[b] Distillation, 50% not above 213° C, dry below 230° C.
[c] Distillation, 20% not above 210° C, dry below 217° C.
[d] Distillation, 5% off between 214 and 217° C, 95% off between 220 and 225° C.
[e] Distillation, 50% above 213° C, dry above 230° C.
[f] Boiling range 200 to 228° C.
[g] Boiling range 221 to 245° C.
[h] Boiling range 248 to 300° C.
[i] Boiling range 210 to 235–240° C maximum.
[j] Boiling range 235 to 260–271° C maximum.
[k] Boiling range 194 to 210° C at 1 mm.
[l] Boiling range 135° C at 10 mm. to 190° C at 4.5 mm.
[m] Boiling range 140° C at 10 mm. to 165° C at 3.5 mm.

The polyhydric phenol sulfides were found to produce reclaims with inferior properties. Reaction products prepared from catechol, resorcinol, hydroquinone, pyrogallol, and phloroglucinol were all poorer than the reaction product of phenol and sulfur monochloride. Various alkyl derivatives of these compounds did not produce any significant increase in softening activity compared with the parent polyhydric phenol.

The comparison was made between 4-*tert*-butyl-3-methylphenol and a number of sulfide reaction products prepared by the variation of the phenol–sulfur monochloride ratio. Very poor softening activity was obtained with unreacted 4-*tert*-butyl-3-methylphenol. The normal reaction product (1.0 mole of 4-*tert*-butyl-3-methylphenol to 0.5 mole of sulfur monochloride) was found to be very effective as a softener. The products obtained by reacting 0.75 or 1.0 mole of sulfur monochloride with 1 mole of 4-*tert*-butyl-3-methyl-

phenol were approximately as active as the normal preparation. However, a higher ratio of sulfur monochloride (1.0 mole of 4-*tert*-butyl-3-methylphenol to 1.25 moles of sulfur monochloride) produced a product of slightly lower activity.

To determine the importance of the sulfide bridge between phenol rings, pure 4-*tert*-butyl-3-methylphenol monosulfide was compared with the corresponding sulfoxide and sulfone. In the same group were compared the crude reaction products prepared from sulfur monochloride and sulfur dichloride. The crude sulfur monochloride reaction product or sulfide mixture was the most effective, being slightly more active than the sulfur dichloride reaction product which, in turn, was slightly more active than the purified monosulfide. A surprising result was that the sulfoxide was slightly more effective, weight for weight, than the monosulfide. The poorest reclaim was obtained from the sulfone. Both sulfoxide and sulfone appeared to be relatively insoluble in the scraps before heating.

The above comparison of the phenol sulfides of different structures makes possible the following generalizations concerning their reclaiming activity.

Reclaiming activity.—Increasing the length of the chain in the monoalkylphenol sulfides was not effective in increasing their activity. The introduction of a second and a third alkyl group into the phenol nucleus produced considerable enhancement of softening ability.

The position of the various alkyl groups on the phenol nucleus was not so important to activity as the number of alkyl groups, as long as one of the ortho- or para-positions was left open for introduction of the sulfide or sulfoxide groups. Phenols with alkyl groups in the 2,4-, 3,4-, 2,3,5-, and 3,4,6-positions formed sulfides in the 2,4-, or 6-positions which were found to be active as reclaiming agents. The 2,4,6-trialkyl substituted compounds, with the ortho- and para-positions filled, reacted with sulfur chloride, but the products were relatively low in reclaiming activity.

The reaction products prepared from the various commercial cresylic acid mixtures indicated that the higher boiling petroleum acids were more active than the lower or higher boiling coal-tar acids. This indicates that the greater number of alkyl groups around the phenol nucleus, which characterizes the higher boiling petroleum acids, contributed greater activity than the larger number of fused ring phenolic compounds found in the higher boiling coal-tar acids.

The reduced ring compounds, the cyclohexanols, like the phenols, are ineffective without substituent alkyl groups. It was interesting to find that the diamylcyclohexanol reaction product was active, almost equal to the corresponding diamylphenol derivative.

The polyhydric phenols and their alkyl derivatives formed sulfur chloride reaction products which were found to be ineffective as reclaiming agents. The introduction of a second and a third hydroxyl group produced compounds with much lower activity than the monohydroxy compounds.

The comparison of the sulfides with the corresponding sulfoxide and sulfone prepared from 4-*tert*-butyl-3-methylphenol provided some very interesting results. The sulfoxide linkage proved to be equivalent to or slightly more active than the monosulfide linkage, whereas the sulfone was practically inert. The crude preparations from sulfur dichloride and from sulfur monochloride, which included a certain proportion of polysulfides in the reaction mixture, were slightly more active than the purified monosulfide.

TABLE III

COMPARISON OF RECLAIMS

	A	B	C	D	E	F
GR-S tread scrap (5-mesh)	100	100	100	100	100	100
Dipentene	6	6	6	6	6	6
Coumarone-indene resin	6	6	6	6	6	6
4,6-Di-*tert*-butyl-3-methyl-phenol sulfide	1.5					
α-Thionaphthol		1.5				
β-Thionaphthol			1.5			
Xylenethiol				3.0		
Zinc salt of xylenethiol					1.5	
Cresol sulfide mixture						1.5

Properties of uncured refined reclaim sheet

	A	B	C	D	E	F
Sheet evaluation						
Thickness (inch)	0.006	0.008	0.011	0.010	0.010	0.013
Body	F⁺-G	F⁺	F	F	F	P-F
Tack	5⁺	4⁺	3⁺	3⁻	3⁺	2⁺
Mooney plasticity values, MS/4/212	41	50	56	55	58	67
Physical tests						
Elongation	300	290	230	220	230	190
Tensile strength	105	135	121	114	123	106
Chemical analysis						
Acetone extract	16.65	16.75	16.47	16.57	16.02	15.95
Ash	3.80	3.80	3.80	3.80	3.80	3.80
Uncured chloroform extract	14.85	12.68	11.75	10.90	11.67	8.27
Carbon black	24.33	24.33	24.33	24.33	24.33	24.33
Total sulfur	1.41	1.50	1.54	1.26	1.37	1.52
Cured chloroform extract	5.03	5.85	3.66	4.86	4.93	3.63
Total rubber hydrocarbon	48.78	47.77	50.20	49.18	49.45	50.77

Properties of cured all-reclaim stocks
Test formula

Reclaim	200.0
Zinc oxide	5.0
Stearic acid	2.0
Sulfur	3.0
Mercaptobenzothiazole	0.5
Diphenylguanidine	0.2

Physical tests

	A	B	C	D	E	F
Cure 20 min. at 287ᵃ F						
300% stress	350	350	375	400	450	675
Elongation	460	470	480	460	460	380
Tensile (lb./sq. inch)	775	875	900	900	925	1000
Shore hardness (D)	43	43	43	44	46	49
Cure 25 min. at 287° F						
300% stress	350	375	400	400	500	725
Elongation	480	480	470	480	440	380
Tensile (lb./sq. inch)	875	950	950	950	950	1125
Shore hardness (D)	43	45	44	46	46	49
Cure 30 min. at 287° F						
300% stress	375	400	400	425	500	800
Elongation	440	480	470	460	420	370
Tensile (lb./sq. inch)	800	925	975	1000	975	1125
Shore hardness (D)	44	45	45	46	46	49

ᵃ 50% solution of xylenethiol in inert hydrocarbon solvent.

PROPERTIES OF RECLAIMS

To obtain a comparison between reclaims produced with the aid of different reclaiming agents, the sulfide mixture prepared from the reaction of sulfur monochloride with 4,6-di-*tert*-butyl-3-methylphenol was compared with a commercial cresol sulfide mixture, α-thionaphthol, β-thionaphthol, xylenethiol, and the zinc salt of xylenethiol, (names of suppliers of commercial products furnished on request). These materials were chosen as active reclaiming agents which have been used in recent years both in this country and abroad.

The data obtained on the uncured refined reclaim sheet (Table III) included the complete chemical analysis, as well as the tensile strength and elongation, determined on small dumbbell strips using the small Scott tensile machine, Mooney plasticity values, and the usual thickness, body, and tackiness ratings. These all agreed in showing that the 4,6-di-*tert*-butyl-3-methylphenol sulfide was the most active reclaiming agent of the group, and produced a thinner reclaim sheet, with the best body and tackiness, the lowest Mooney plasticity value (MS/4/212), the greatest elongation and lowest tensile strength, and the highest uncured chloroform extract. The cresol sulfide mixture was

TABLE IV

EFFECT OF CONCENTRATION OF RECLAIMING AGENT

	A	B	C	D	E	F
GR-S tread scrap (5-mesh)	100	100	100	100	100	100
Swelling agent and tackifier	12.0	11.5	11.0	10.0	8.0	4.0
4,6-Di-*tert*-butyl-3-methyl- phenol sulfide		0.5	1.0	2.0	4.0	8.0
Sheet evaluation						
Thickness (inch)	0.013	0.011	0.008½	0.008	0.007	0.006
Body	P-T	F	G	G	VG	Oversoft
Tackiness	2+	3+	5+	6+	7+	8+
Chemical analysis						
Acetone extract	19.45	18.15	18.63	17.93	18.45	22.75
Uncured chloroform extract	7.35	8.68	10.40	11.33	11.48	14.70
Cured chloroform extract	1.45	1.71	1.66	2.13	2.71	3.42

the least active of the series, with the other materials intermediate in activity. The various physical tests on the uncured reclaim sheet agree remarkably well in rating the different reclaims.

The physical properties of the vulcanized reclaims do not vary as widely as those of the uncured reclaim sheets. The poor, rather nonuniform reclaim sheet prepared using the cresol sulfide mixture had both low elongation and tensile strength; the vulcanized reclaim showed both high modulus and tensile coupled with low elongation. The vulcanized reclaim prepared from 4,6-di-*tert*-butyl-3-methylphenol sulfide exhibited consistently lower modulus and tensile strength, together with equivalent elongation, compared to the reclaim vulcanizates from the arylthiols. This is taken to be an indication of a greater degree of breakdown produced by the 4,6-di-*tert*-butyl-3-methylphenol sulfide.

Table IV shows some effects on the reclaim sheet, produced by increasing the concentration of reclaiming agent. A total content of 12 parts of softener plus reclaiming agent per hundred of scrap was maintained during the study. The reclaim made from the addition of swelling agent alone had the lowest cured and uncured chloroform extracts. With the reclaiming agent present in

concentrations of 0.5, 1.0, and 2.0 parts, the quality of the reclaim improved considerably and both chloroform extracts increased. Higher concentrations— e.g., 4.0 and 8.0 parts of reclaiming agent—produced reclaims which were very soft and, therefore, of less desirable workability. The chloroform extract of these reclaims again showed a significant increase.

The acetone extracts did not follow the chloroform extracts, and actually decreased slightly with increasing reclaiming agent. However, the largest amount of reclaiming agent used, 8 parts, did cause an increase in the acetone extract of the product.

The increase in the chloroform extracts with increasing reclaiming agent concentration is very interesting. It indicates that an increase in the amount of lower molecular-weight fragments from the GR-S vulcanizate is produced with an increase in the amount of reclaiming agent used. The cured chloroform extract is generally thought to represent segments of the vulcanized rubber structure which have been degraded to such an extent that they do not readily revulcanize[13].

PHENOL SULFIDES AS RECLAIMING AGENTS FOR OTHER SYNTHETIC RUBBERS

The sulfides of 4,6-di-*tert*-butyl-3-methylphenol were found to be active for reclaiming several other types of synthetic rubbers such as the butadiene-acrylonitrile copolymers (N types) and Neoprene. Table V reports the comparison of this highly alkylated phenol sulfide with the thiol type of softeners. The degree of activity of the phenol sulfide softener in these rubbers is not as great as in GR-S type scraps. This may be due in part to the fact that the large amounts of oils and tackifiers, which were necessarily used to swell and

TABLE V

PHENOL SULFIDES AS RECLAIMING AGENTS FOR
OTHER SYNTHETIC RUBBERS

	A	B	C
N type synthetic rubber scrap (5-mesh)	100	100	100
Oils and tackifiers	35	35	35
4,6-Di-*tert*-butyl-3-methylphenol sulfide	2.0		
α-Thionaphthol[a]		2.0	
Zinc salt of xylenethiol[b]			2.0
Sheet evaluation			
Thickness (inch)	0.017	0.020	0.020
Body	G	G	G
Tackiness	3+	2+	2+
Neoprene scrap (5-mesh)	100	100	100
Oils and tackifiers	35	35	35
4,6-Di-*tert*-butyl-3-methylphenol sulfide	3.0		
α-Thionaphthol[a]		5.0	
Zinc salt of xylenethiol[b]			5.0
Sheet evaluation			
Thickness (inch)	0.021	0.023	0.023
Body	V-G	G	G
Tackiness	6+	6+	5+

[a] 50% solution of α-thionaphthol in inert hydrocarbon solvent.
[b] 50% solution of zinc salt of xylenethiol in inert hydrocarbon solvent.

plasticize the vulcanized scrap, masked some of the action of the chemical softener.

The use of highly alkylated phenol sulfides in reclaiming these oil-resistant polymers is very beneficial.   Without them, even greater amounts of oil would be necessary to produce a satisfactory reclaim.   The alkylphenol sulfides, therefore, produce from these scraps reclaims which have higher rubber contents and lower acetone extracts than it has heretofore been possible to obtain.

The alkylated phenol sulfides are even more active for the reclaiming of natural rubber than for the synthetic rubbers.

FATE OF COMBINED SULFUR AND RECLAIMING AGENT DURING THE RECLAIMING PROCESS

The vulcanization of rubber by sulfur is only partly understood; nevertheless, it certainly involves the chemical reaction of rubber hydrocarbon chains with sulfur and the joining of these chains to form a cross-linked structure. Soft vulcanized rubber, even in the presence of antioxidants, is more or less readily attacked by the oxygen of the air, being only slightly more resistant to attack than the corresponding unvulcanized rubber.   Aged vulcanized scrap, the usual raw material of the reclaim industry, therefore consists of a cross-linked hydrocarbon chain structure containing both chemically combined sulfur and oxygen.

The reclaiming process is frequently referred to as devulcanization.   In the sense that a stiff, hard, high modulus, nonprocessible vulcanizate is converted during the reclaiming process to a soft, plastic, more tacky, low modulus, processible, and vulcanizable product having many of the properties of the original rubber, the term devulcanization is appropriate.   However, in the chemical sense it has been generally recognized that the reclaiming process does not reverse the chemical reactions taking place during vulcanization. Chemically speaking, therefore, the so-called devulcanization process, involving the separation of combined sulfur from the rubber hydrocarbon, does not take place in the usual reclaiming processes[14].

In this connection it was of interest to examine the effect of the most active reclaiming agents with respect to the fate of the sulfur, particularly the combined sulfur in the vulcanized scrap, during the reclaiming process.   In fact, the hypothesis may be advanced that the phenol sulfides, particularly those prepared from sulfur monochloride, might act through a monosulfide-polysulfide equilibrium.   At temperatures below 150° C, it has been shown that these materials may furnish polysulfide sulfur to the rubber hydrocarbon[15].   At temperatures above 175° C, it might be postulated that these sulfides could remove sulfur from the vulcanized rubber.

As a result of this speculation, the authors have determined the combined sulfur, before and after reclaiming, of four carefully controlled and reclaimed samples: A, a nonsulfur-cured GR-S, and B, C, and D, three samples of a typical sulfur-cured GR-S (Table VI).

One of these samples, D, was acetone-extracted before analysis and reclaiming.   A small amount of combined sulfur was found in the nonsulfur-cured stock, and this must have been introduced with the GR-S polymer, the carbon black or the zinc oxide, for it was common to all the stocks.   The nonsulfur-cured GR-S, A, and two of the sulfur-cured samples, including that which was acetone-extracted, C and D, were reclaimed by the usual procedure in the presence of 1.50 parts per 100 parts of scrap of pure 4,6-di-*tert*-butyl-3-methyl-

TABLE VI

FATE OF SULFUR DURING RECLAIMING OF GR-S

Formulas	Anal. data	A Composition and analysis	A Sulfur calcd. as % of total stock
		GR-S vulcanizates used as scraps for reclaiming	
GR-S		100.00	
Carbon black (EPC)		45.00	
Zinc oxide		2.40	
Softeners and antioxidant		10.10	0.010
Total sulfur, determined: 0.18%; 0.14%			
Dibenzoylquinone dioxime		5.00	
Sulfur		..	
N-Cyclohexyl-2-benzothiazole sulfenamide		..	
		162.50	0.010

Chemical analysis			
Acetone extract (16 hours)		10.9% of vulcanizate	
Total sulfur in GR-S vulcanizate	0.15		
	0.17	0.16% of vulcanizate	
Total sulfur in acetone extract	0.24% of extract	0.026% of vulcanizate	
Sulfur combined with GR-S		0.13% of vulcanizate	
Combined sulfur in vulcanizate per 100 parts of GR-S		0.211	

Formulas	Anal. data	Reclaims A Composition and analysis	Reclaims A Sulfur calcd. as % of total stock
GR-S vulcanizate		100.00	0.149
Cumar 2½ MH } Total sulfur detd.: 0.28%; 0.31%		6.00 }	0.033-
Solvenol		6.00 }	
4,6-Di-tert-butyl-3-methylphenol monosulfide. % S = 6.82		1.50	0.095
		113.50	
Solvenol volatilized during reclaiming		−6.00	
		107.50	0.277

Chemical analysis			
Acetone extract (16 hours)		16.2% reclaim	
Total sulfur in GR-S reclaim	0.23		
	0.24	0.235% of reclaim	
Total sulfur in acetone extract	0.43% of extract		
	0.44% of extract	0.070% of reclaim	
Sulfur combined with GR-S reclaim		0.165% of reclaim	
Combined sulfur in reclaim per 100 parts of GR-S		0.288	
Gain or loss in combined sulfur during reclaiming per 100 parts of GR-S		+0.077	
Sulfur added as 4,6-di-tert-butyl-3-methylphenol monosulfide reclaiming agent per 100 parts of GR-S		0.166	
Reclaiming agent combined with GR-S from sulfur analysis (%)		47	
Free sulfur in acetone extract by sulfite method (%)	0.002		
	0.000	0.001	
Combined sulfur in acetone extract corrected for sulfur in Cumar and Solvenol		0.036% of reclaim	
Sulfur added as 4,6-di-tert-butyl-3-methylphenol monosulfide reclaiming agent per 100 parts of reclaim		0.095	
Reclaiming agent recovered in acetone extract from sulfur analysis (%)		38	
Total reclaiming agent accounted for by sulfur analyses (%)		85	

TABLE VI.—*Continued*

Formulas	Anal. data	B Composition and analysis	B Sulfur calcd. as % of total stock
		GR-S vulcanizates used as scraps for reclaiming	
GR-S		100.00	
Carbon black (EPC)		45.00	
Zinc oxide		2.40	
Softeners and antioxidant		10.10	0.010
Total sulfur, determined: 0.18%; 0.14%;			
Dibenzoylquinone dioxime		..	
Sulfur		1.70	1.059
N-Cyclohexyl-2-benzothiazole sulfenamide		1.20	0.181
		160.40	1.250

Chemical analysis

	Anal. data		
Acetone extract (16 hours)			8.0% of vulcanizate
Total sulfur in GR-S vulcanizate	1.40 1.38		1.40% of vulcanizate
	1.40 1.42		
Total sulfur in acetone extract	0.11% of extract		0.009% of vulcanizate
Sulfur combined with GR-S			1.391% of vulcanizate
Combined sulfur in vulcanizate per 100 parts of GR-S			2.233

Reclaims

	Anal. data	B Composition and analysis	B Sulfur calcd. as % of final reclaim
GR-S vulcanizate		100.00	1.320
Cumar 2½ MH } Total sulfur detd.: 0.28%; 0.31%		6.00 }	0.033+
Solvenol		6.00 }	
4,6-Di-*tert*-butyl-3-methylphenol monosulfide. % S = 6.82		..	..
		112.00	
Solvenol volatilized during reclaiming		−6.00	
		106.00	1.353

Chemical analysis

	Anal. data		
Acetone extract (16 hours)			12.9% of reclaim
Total sulfur in GR-S reclaim	1.32		1.335% of reclaim
	1.35		
Total sulfur in acetone extract	0.64% of extract		0.083% of reclaim
	0.65% of extract		
Sulfur combined with GR-S reclaim			1.252% of reclaim
Combined sulfur in reclaim per 100 parts of GRS-			2.128
Gain or loss in combined sulfur during reclaiming per 100 parts of GR-S			−0.105
Sulfur added as 4,6-di-*tert*-butyl-3-methylphenol monosulfide reclaiming agent per 100 parts of GR-S			..
Reclaiming agent combined with GR-S from sulfur analysis (%)			..
Free sulfur in acetone extract by sulfite method (%)	0.039 0.023		
	0.027 0.027		0.027
Combined sulfur in acetone extract corrected for sulfur in Cumar and Solvenol			0.023% of reclaim
Sulfur added as 4,6-di-*tert*-butyl-3-methylphenol monosulfide reclaiming agent per 100 parts of reclaim			..
Reclaiming agent recovered in acetone extract from sulfur analysis (%)			..
Total reclaiming agent accounted for by sulfur analyses (%)			..

TABLE VI.—*Continued*

		C	
Formulas	Anal. data	Composition and analysis	Sulfur calcd. as % of total stock
	GR-S vulcanizates used as scraps for reclaiming		
GR-S		100.00	
Carbon black (EPC)		45.00	
Zinc oxide		2.40	
Softeners and antioxidant		10.10	0.010
Total sulfur, determined: 0.18%; 0.14%			
Dibenzoylquinone dioxine		. .	
Sulfur		1.70	1.059
N-Cyclohexyl-2-benzothiazole sulfenamide		1.20	0.181
		160.40	1.250

Chemical analysis			
Acetone extract (16 hours)		8.0% of vulcanizate	
Total sulfur in GR-S vulcanizates	1.40 1.38		
	1.40 1.42	1.40% of vulcanizates	
Total sulfur in acetone extract	0.11% of extract	0.009% of vulcanizate	
Sulfur combined with GR-S		1.391% of vulcanizate	
Combined sulfur in vulcanizate per 100 parts of GR-S		2.233	

		Reclaims	
		C	
Formulas	Anal. data	Composition and analysis	Sulfur calcd. as % of final reclaim
GR-S vulcanizate		100.00	1.302
Cumar 2½ MH	Total sulfur detd.: 0.28%; 0.31%	6.00 }	0.033⁻
Solvenol		6.00	
4,6-Di-tert-butyl-3-methylphenol monosulfide. % S = 6.82		1.50	0.095
		113.50	
Solvenol volatilized during reclaiming		−6.00	
		107.50	1.430

Chemical analysis			
Acetone extract (16 hours)	1.43	13.4% of reclaim	
Total sulfur in GR-S reclaim	1.44	1.435% of reclaim	
Total sulfur in acetone extract	0.67% of extract	0.103% of reclaim	
	0.87% of extract		
Sulfur combined with GR-S reclaim		1.332% of reclaim	
Combined sulfur in reclaim per 100 parts of GR-S		2.296	
Gain or loss in combined sulfur during reclaiming per 100 parts of GR-S		+0.063	
Sulfur added as 4,6-di-tert-butyl-3-methylphenol monosulfide reclaiming agent per 100 parts of GR-S		0.164	
Reclaiming agent combined with GR-S from sulfur analysis (%)		. .	
Free sulfur in acetone extract by sulfite method (%)	0.013		
	0.031	0.028	
	0.039		
Combined sulfur in acetone extract corrected for sulfur in Cumar and Solvenol		0.042% of reclaim	
Sulfur added as 4,6-di-tert-butyl-3-methylphenol monosulfide reclaiming agent per 100 parts of reclaim		0.095	
Reclaiming agent recovered in acetone extract from sulfur analysis (%)		. .	
Total reclaiming agent accounted for by sulfur analyses (%)		. .	

TABLE VI.—*Continued*

		D	
Formulas	Anal. data	Composition and analysis	Sulfur calcd. as % of total stock
		GR-S vulcanizates used as scraps for reclaiming	
GR-S		100.00	
Carbon black (EPC)		45.00	
Zinc oxide		2.40	
Softeners and antioxidant		10.10	0.010
Total sulfur, determined: 0.18%; 0.14%			
Dibenzoylquinone dioxime			
Sulfur		1.70	1.059
N-Cyclohexyl-2-benzothiazole sulfenamide		1.20	0.181
		160.40	1.250
		Vulcanizate acetone-extracted before analysis	
		Formula weight (calcd.) after extraction	
		149.6	1.34
Chemical analysis			
Acetone extract (16 hours)		1.36% of vulcanizate	
Total sulfur in GR-S vulcanizate	1.41		
	1.43	1.42% of vulcanizate	
Total sulfur in acetone extract	0.14% of extract		
	0.20% of extract	0.002% of vulcanizate	
Sulfur combined with GR-S		1.418% of vulcanizate	
Combined sulfur in vulcanizate per 100 parts of GR-S		2.121	

		Reclaims D	
Formulas	Anal. data	Composition and analysis	Sulfur calcd. as % of final reclaim
GR-S vulcanizate		100.00	1.323
Cumar 2½ MH } Total sulfur detd.: 0.28%; 0.31%		6.00 }	0.033-
Solvenol		6.00 }	
4,6-Di-*tert*-butyl-3-methylphenol monosulfide.		1.50	0.095
% S = 6.82			
		113.50	
Solvenol volatilized during reclaiming		−6.00	
		107.50	1.451
Chemical analysis			
Acetone extract (16 hours)		9.3% of reclaim	
Total sulfur in GR-S reclaim	1.45		
	1.46	1.455% of reclaim	
Total sulfur in acetone extract	0.63% of extract		
	0.71% of extract	0.073% of reclaim	
	1.01% of extract		
Sulfur combined with GR-S reclaim		1.382% of reclaim	
Combined sulfur in reclaim per 100 parts of GR-S		2.222	
Gain or loss in combined sulfur during reclaiming per 100 parts of GR-S		+0.101	
Sulfur added as 4,6-di-*tert*-butyl-3-methylphenol monosulfide reclaiming agent per 100 parts of GR-S		0.153	
Reclaiming agent combined with GR-S from sulfur analysis (%)		66	
Free sulfur in acetone extract by sulfite method(%)	0.012 0.005		
	0.007 0.007	0.008	
Combined sulfur in acetone extract corrected for sulfur in Cumar and Solvenol		0.032% of reclaim	
Sulfur added as 4,6-di-*tert*-butyl-3-methylphenol monosulfide reclaiming agent per 100 parts of reclaim		0.095	
Reclaiming agent recovered in acetone extract from sulfur analysis (%)		34	
Total reclaiming agent accounted for by sulfur analyses (%)		100	

phenol monosulfide. Sample B was treated in exactly the same manner, but without the addition of the alkyl phenol sulfide reclaiming agent.

In each vulcanizate the difference between the total sulfur in the sample and the total sulfur in the acetone extract was taken as the sulfur actually combined with the GR-S polymer. These differences were calculated to the basis of the 100 parts of GR-S used in the preparation of the original vulcanizate. They show that the three samples reclaimed in the presence of the sulfide reclaiming agent actually gained about 0.1 per cent of sulfur combined per 100 parts of polymer during the reclaiming process, whereas a small amount of sulfur was actually removed from the stock treated in the absence of reclaiming agent. These differences are small, but they are larger than the probable errors involved in their calculation, and the excellent internal agreement shown in this series of analyses lends weight to the conclusion that during this reclaiming process, a vulcanizate containing the alkylphenol sulfide reclaiming agent shows an increase in combined sulfur relative to a vulcanizate treated without the reclaiming agent.

TABLE VII

NONSULFUR-CURED AND SULFUR-CURED RECLAIMS PRODUCED
FOR ANALYSIS (TABLE VI)

	A	B	C	D
				Sulfur-cured GR-S
	Nonsulfur-cured GR-S	Sulfur-cured GR-S	Sulfur-cured GR-S	acetone extracted
GR-S tread scrap	100.0	100.0	100.0	100.0
Oils and tackifiers	12.0	12.0	12.0	12.0
4,6-Di-*tert*-butyl-3-methylphenol monosulfide	1.5	..	1.5	1.5
Sheet evaluation				
Thickness (one pass) (inch)	0.021	0.031	0.014	0.024
Body	P	P-T	G	P-F
Tackiness	2⁻	3⁻	6	3⁺

In fact, in the stocks which contained no free sulfur at the start of the reclaiming process, it may be postulated that increase in combined sulfur must represent reclaiming agent (or molecular fragments from its reactions) which has combined with the polymer vulcanizate during the process. Such a calculation was made for stocks A and D (Table VI) and showed 47 and 66 per cent, respectively, of the reclaiming agent sulfur combined with the vulcanizate during the reclaiming process. If some of the reclaiming agent combines with the polymer during reclaiming, then the remainder should be recoverable in the acetone extract of the reclaimed samples. This calculation also was made, after correcting the total sulfur in the acetone extract for free sulfur (determined by the sulfite method[16]), and for sulfur added with the reclaiming oils and tackifiers. The results show a recovery of 38 and 34 per cent, respectively, of the reclaiming agent sulfur in the acetone extracts from reclaims A and D. The sum of the sulfur combined and the sulfur recovered in the acetone extract accounts very satisfactorily for the sulfur introduced into the process as reclaiming agent. It is obvious that these figures are not by any means absolute. However, the values obtained appear to be significant, and certainly the trends are significant. It may then be concluded that in vulcanizates reclaimed with the aid of the alkylphenol sulfide reclaiming agent, part of the sulfur introduced

as reclaiming agent combines with the vulcanizate during the reclaiming process, and the remainder is recoverable in the acetone extract of the finished reclaim.

The preceding analyses make untenable the sulfur equilibrium hypothesis, and another mechanism for the activity of these reclaiming agents must be sought.

The evaluation of the reclaims produced for the analyses of Table VI is shown in Table VII. This illustrates the importance of the acetone-soluble oils and plasticizers which were lacking in sample D, and also shows that the alkylphenol sulfide reclaiming agent was effective in the nonsulfur-cured vulcanizate. This last observation was extended to a higher concentration of reclaiming agent in GR-S, and also to a nonsulfur-cured Butyl rubber vulcanizate in Tables VIII and IX.

TABLE VIII
NONSULFUR-CURED GR-S RECLAIMS

	A	B	C
Dibenzo GMF[a] cured GR-S tread scrap	100.0	100.0	100.0
Oils and tackifiers	12.0	12.0	12.0
4,6-Di-*tert*-butyl-3-methylphenol monosulfide	..	1.5	3.0
Sheet evaluation			
Thickness (inch)	0.036	0.018	0.013
Body	P-L-T	P-L-T	F-G
Tackiness	0	3⁻	5⁻

[a] Dibenzoyl quinone dioxime.

TABLE IX
NONSULFUR-CURED BUTYL RECLAIMS

	Formula without alkyl phenol sulfide	Formula with 2 parts 4,6-di-*tert*-butyl-3-methylphenol sulfide
Body	V-P-T	F-G
Tackiness	2⁻	6

From the data cited in Tables VI to IX, inclusive, it may be concluded that carbon-carbon bonds, rather than carbon-sulfur bonds are mainly affected in the vulcanizate during this reclaiming process.

CONCLUSIONS CONCERNING MECHANISM OF RECLAIMING PROCESS

A study of the literature on reclaiming leads to the almost inevitable conclusion that the oxidative scission of polymer vulcanizates plays a predominant role in most of the reclaiming processes. The reclaiming temperatures used in the present experiments were below those at which appreciable thermal depolymerization or cracking (natural rubber) occurs in the absence of oxygen[17]. Cyclization, except in so far as it is an adjunct of the oxygen and reclaiming agent attack, probably can be ruled out as the main reaction by the known resistance of vulcanized rubber to cyclizing agents, even at elevated temperatures, and by the lack of properties generally associated with cyclized rubber products—*e.g.*, hardness, thermoplasticity, low elongation, and loss of chemical activity.

The effect of the oxygen concentration on the speed and extent of the reclaiming processes for both natural and synthetic rubbers is well known[18].

Probably every reclaim manufacturer has demonstrated that oxygen introduced under pressure will hasten the reclaiming of natural and synthetic rubbers.   An appropriate quotation may be taken from the first page of a German report on the Renacit reclaiming agents[19].

Especially, the former view to the effect that the reclaiming would be due to a desulfurization of the vulcanizates under the influence of alkali has proved to be untenable.   In the past ten years experts in different countries have come to the conclusion that, on reclaiming vulcanized rubber, as well as on plasticizing crude rubber, the decisive part is acted by oxygen, whereas softeners, heating, and mechanical working exert only an accelerating effect. Acids and alkalies merely serve for destroying the fabric.

The process for the reclaiming of Buna synthetic rubbers, as developed by I. G. Farbenindustrie A.-G., included the use of aromatic thiols to accelerate the oxidizing process and the use of air at 2 to 3 atmospheres' pressure to increase the oxygen concentration[19].

Other evidence that oxygen and oxidation are fundamentally involved in the reclaiming process may be deduced from the well known fact that well-aged, oxidized vulcanized scrap is much more susceptible to reclaiming than fresh unoxidized rubber vulcanizate[20]; also, that as the proportion and effectiveness of antioxidants (and of accelerators showing strong antioxidant effects) are increased, the vulcanizate becomes increasingly difficult to reclaim successfully[21].

If we can assume that the fundamental reaction of the usual reclaiming processes is oxidative in nature, it is natural to conclude that alkylphenol sulfide reclaiming agents are catalysts for the oxidative scission reactions of rubber hydrocarbons and vulcanizates, while remaining inert to, or actually inhibiting, the oxidative aggregation reactions which are known to take place simultaneously during the oxidation of both natural and synthetic hydrocarbon polymers[22].   The reactions of hydrocarbon chains with oxygen are generally believed to proceed through radical chain mechanisms, and these reclaiming agents themselves may act by the formation of radicals or fragments which may aid in the oxidative breakdown, perhaps by aiding the dehydrogenation of the polymer chains and also by reaction with the fragments formed.   Alkylphenol sulfides may help to prevent oxygen-catalyzed aggregation in the same manner by which similarly alkylated phenols protect synthetic polymers and vulcanizates (N and GR-S types) from aggregation or stiffening during natural and accelerated aging [23].

In connection with the above ideas the following facts may be considered significant:

Both thiols and disulfides are known to catalyze oxidation or dehydrogenation reactions, presumably through free radical mechanisms[24].

An increase in oxygen pressure is reported to increase the plasticity and quality of a Buna-S reclaim in the presence of an aryl thiol reclaiming agent[19].

The alkylphenol sulfoxides and sulfides, which are relatively less stable under reclaiming conditions, are much more active than the corresponding sulfones which contain more oxygen but are very stable compounds.

The increase in the chloroform extracts of the uncured reclaims with increase in the amount of reclaiming agent used suggests the formation of polymer vulcanizate fragments of low molecular weight.

The activity of the alkylphenol sulfide reclaiming agents in several different polymer vulcanizates (GR-S, butadiene-acrylonitrile copolymers, Neoprene, Butyl), cured with or without sulfur, suggests that the reactivity must center

on the only common functional groups in these materials—that is, the hydro-carbon chains of the original polymers.

Further work is indicated to prove the relationship of the alkylphenol sulfides and of oxygen in the usual reclaiming processes.

SUMMARY

Some highly alkylated phenol sulfides have proved to be among the most active reclaiming agents for GR-S and other synthetic rubbers.

A study has been made of the activities of these materials as related to molecular structure and to the fate of sulfur during the reclaiming process.

The nature and mechanism of the chemical reactions taking place during the reclaiming of natural and synthetic rubbers have been discussed in the light of the results obtained.

ACKNOWLEDGMENT

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SEMIEBONITES*

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Semiebonites are compounds with properties between soft and hard rubber which are formed by vulcanizing with medium percentages of sulfur. The term semiebonite is used to define these compounds, rather than the often synonymously used term semihard rubber, since leathery semihard rubber compounds can be produced also by high filler loadings and by compounding with resins. This paper deals only with semiebonites whose properties are obtained by sulfur.

When rubber hydrocarbons are vulcanized with increasing percentages of sulfur, three properties of the vulcanizate change in proportion to the percentage of sulfur: hardness, elongation, and elasticity. The hardness increases; the elongation and elasticity decrease. The appearance and the feeling of the vulcanizate change gradually from soft and elastic to hard and rigid through the intermediate range of leathery properties. These changes in properties of the vulcanizate are shown schematically in Figure 1. A strict definition of the borderlines is neither necessary nor possible. To define the subject of this paper, the range between 10 sulfur and 25 sulfur is labeled the semiebonite range. This is more or less in accordance with general practice.

The hardness range of the compounds in the semiebonite range, as defined, is approximately between 40 and 90 Shore-A durometer reading and the elongation at break, between 20 and 300 per cent. This combination of medium to high hardness with low to medium elongation and low elasticity gives the compounds in the medium sulfur range their leathery appearance.

The semiebonite range of rubber compounds has always been a stepchild of rubber compounders. Although the literature on rubber is very voluminous, it is only seldom that we come across a reference dealing with semiebonite. There are, of course, good reasons for this fact. The principal one is that the rubber compounders' and consumers' experience with this type of vulcanizates has been, as a rule, one of disappointment. As with all rubber compounding knowledge, the basic facts and principles are derived from studies of natural rubber. The fact that vulcanizates of natural rubber in the semiebonite range have poor physical properties and extremely poor aging characteristics has deterred the majority of rubber chemists from spending time on investigating this field. Semiebonites made from natural rubber show the well known deteriorations which start with a glossy, hard-skin formation, followed by progressive hardening and cracking on bending. Gibbons[1] describes in detail the properties of semiebonites from natural rubber. A condensed discussion of these properties with literature references has been given by Cotton[2].

PURPOSE OF THE PAPER

This paper reports an investigation carried out for the purpose of comparing the behavior of modern synthetic rubbers with that of natural rubber through
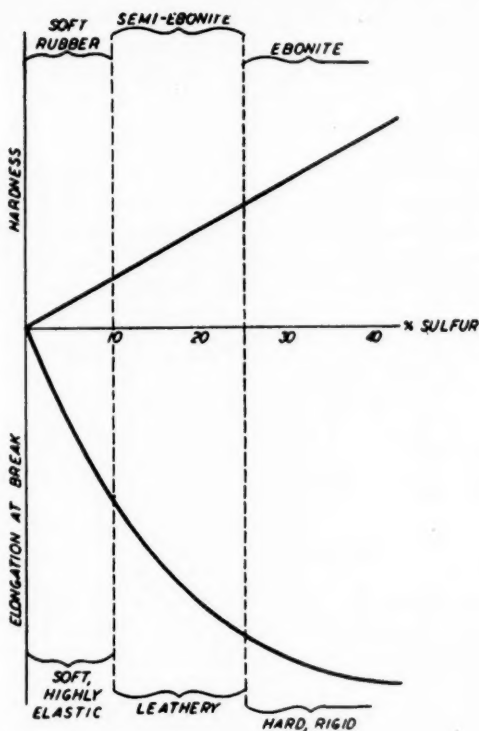
Fig. 1.—Sulfur ranges.

the whole range of sulfur from soft rubber to ebonite. The results of this investigation appear sufficiently interesting to warrant presentation. The investigation was merely a general study and was not aimed at developing any particular compound. However a great number of compounds have been tested, and some of the data presented may be useful as starting points for compound development.

SCOPE OF INVESTIGATION

A natural rubber (smoked sheet), a butadiene-styrene rubber (GR-S), and a butadiene-acrylonitrile rubber (Hycar OR-25) were compounded with increasing percentages of sulfur to give a whole range of vulcanizates from soft rubber to ebonite. Three basic test formulas were used, a pure-gum compound, an SRF black compound, and a clay compound. Test compounds were made to investigate the influence of unsaturated hydrocarbon extenders. Since the aging characteristics of the rubbers themselves were under investigation, no antioxidants were used in the compounds.

The compounds were mixed and their stress-strain properties were measured by A.S.T.M. procedures before and after aging in air at elevated temperatures. The aging conditions, 48 hours at 100° C, were found to be most practical for this investigation. Some of the compounds were aged seven days in the Geer oven. The more severe aging conditions, 48 hours at 100° C, were later adopted for the purpose of speeding up the investigation.

The plasticities were determined with a Scott parallel-plate plastometer. The figures reported are the compression in 0.001-inch during a 2½-minute compression period, using 15 pounds' load on the spindle and a temperature of 212° F in the platens. Test-specimens were cylindrical, plied-up samples, having original dimensions of $1\frac{7}{16}$ inches in diameter and somewhat more than 0.6 inch in height, and were initially compressed in the plastometer to 0.600 inch in a preliminary half-minute warm-up period before starting the test.

A number of cures were made of each compound. The cures which showed little increase in modulus and hardness on prolonged curing and which showed no sulfur bloom were chosen as optimum cures. This latter consideration is especially important in compounds containing high percentages of sulfur.

A great number of tests were made. The most characteristic results, which illustrate the findings, are given and discussed below.

TABLE 1

Compound No.	1	2	3	4
Smoked sheet rubber	100	100	100	100
Stearic acid	1	1	1	1
Sulfur	15	15	15	15
Zinc oxide	5	5	5	5
Naftolen R100*	—	35	35	35
Suprex clay*	—	—	—	105
Pellex*	—	—	105	—
Benzothiazoyl disulfide	1.2	1.2	1.2	1.2
Diphenylguanidine	0.2	0.2	0.2	0.2
Plasticity (compression in 0.001-in.)	380	465	365	420
Optimum cure at 80 lbs. (min.)	65	35	35	65
Shore hardness (30 sec.)				
Initial	49	36	73	56
Aged 48 hrs. 100° C	47	34	82	76
Tensile strength at break (lbs. per sq. in.)				
Initial	330	250	1820	1120
Aged 48 hrs. 100° C	400	320	800	490
Elongation at break (%)				
Initial	250	260	210	450
Aged 48 hrs. 100° C	300	370	50	60

* The filler and the extender were incorporated in the form of premixed preparations containing 75% filler and 25% extender.

THE BEHAVIOR OF NATURAL RUBBER

The three series of compounds reported in Tables 1, 2, and 3 demonstrate the behavior of natural rubber. In Table 1 are reported the results on four compounds in the medium sulfur range, a pure-gum compound, a compound containing an unsaturated hydrocarbon extender, a compound containing the unsaturated hydrocarbon extender and SRF black, and a compound containing the unsaturated hydrocarbon extender and clay. The clay and SRF black were incorporated in the form of premixed preparations with the extender. This method of compounding was used to facilitate handling and to shorten the mixing time. The principles of this mixing procedure have been described in a previous paper[3]. The compounds were vulcanized for 15 and 35 minutes at 45 pounds and for 35, 65, 90, and 120 minutes at 80 pounds. The cures compared in this table are those which were the first ones in the series of cures without sulfur bloom, indicating that most of the sulfur had combined. The poor aging characteristics of these natural-rubber compounds are clear from the physical test data.

TABLE 2

Compound No.	1		2		3		4	
Smoked sheet rubber	100		100		100		100	
Stearic acid	1		1		1		1	
Sulfur	15		15		15		15	
Zinc oxide	5		5		5		5	
Naftolen R100*	—		35		35		35	
Suprex clay*	—		—		—		105	
Pelletex*	—		—		105		—	
Mercaptobenzothiazole	0.5		0.5		0.5		0.5	
Plasticity (compression in 0.001-in.)	340		432		370		410	
Cure—time (min.)	50	35	50	20	50	35	50	35
Temperature (lbs. steam)	80	35	80	35	80	35	80	35
Shore hardness (30 sec.)								
Initial	49	40	36	30	69	66	58	44
Aged 48 hrs. 100° C	—	43	—	30	—	66	—	36
Tensile strength at break (lbs. per sq. in.)								
Initial	250	2580	270	1700	1660	1920	1020	1530
Aged 48 hrs. 100° C	—	130	—	130	—	1020	—	400
Elongation at break (%)								
Initial	160	720	280	730	230	400	350	590
Aged 48 hr. 100° C	—	160	—	240	—	150	—	260

* The filler and the extender were incorporated in the form of premixed preparations containing 75% filler and 25% extender.

TABLE 3

Compound No.	1	2	3	4	5
Smoked sheets rubber	100	100	100	100	100
Stearic acid	1	1	1	1	1
Sulfur	2	10	15	20	40
Zinc oxide	5	5	5	5	5
Naftolen R100*	35	35	35	35	35
Suprex clay*	105	105	105	105	105
Benzothiazoyl disulfide	1.2	1.2	1.2	1.2	1.2
Diphenylguanidine	0.2	0.2	0.2	0.2	0.2
Plasticity (compression in 0.001-in.)	415	415	425	410	425
Optimum cure—(time in min.)	15	65	65	65	90
Temperature (lbs. steam)	45	80	80	80	80
Shore hardness (30 sec.)					
Initial	38	43	56	69	85†
Aged 48 hrs. 100° C	48	63	76	84	86†
Tensile strength at break (lbs. per sq. in.)					
Initial	1800	1010	1120	1530	4600
Aged 48 hrs. 100° C	1600	300	490	790	4300
Elongation at break (%)					
Initial	600	560	450	270	1
Aged 48 hrs. 100° C	570	100	60	50	1

* The filler and the extender were incorporated in the form of a premixed preparation containing 75% filler and 25% extender.
† D durometer reading.

Table 2 shows the same compounds as in Table 1, but with lower acceleration and two different cures—a high one and a low one. The findings in the work reported in Table 1 are confirmed by the results given in Table 2, that is, the poor aging properties of these compounds are due to the inherent lack of resistance of natural rubber to such aging, and are not caused by conditions of

vulcanization.   The data in this table show that the same low physical proper-
ties are finally obtained by curing to the stage where no sulfur bloom occurs,
or by aging the undercured compounds.   The compounds reported in this
table were cured 15, 20, 35, 50, 80, and 120 minutes at 35 pounds; 20, 35, 50,
and 65 minutes at 45 pounds; and 5, 10, 20, and 50 minutes at 80 pounds.   The
complete test data are plotted in Figure 2.   This graph shows more clearly
than the table the sensitivity of natural rubber-medium sulfur compounds to
the time and temperature of curing.   The high values for the low cures demon-
strate only that the sulfur has not combined, as revealed also by the heavy
sulfur bloom on the test-specimens.   Longer cures, as well as aged properties,
show that natural-rubber compounds with medium percentages of sulfur are
valueless.

Table 3 presents a series of smoked-sheet compounds with increasing per-
centages of sulfur, based on Compound 4 given in Table 1.   The data are dis-
cussed later in connection with Figure 4.
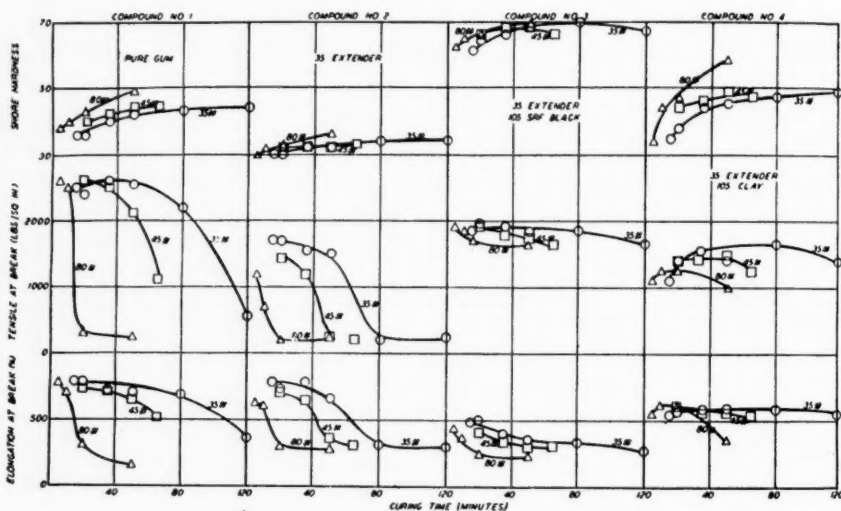
Fig. 2.—Variation of cure on natural rubber semiebonite.

Table 4 reports tests made on reclaimed natural rubber, using the same
formulations as with the smoked sheet compounds presented in the foregoing
Tables 1 and 3.   The first five compounds show the influence of increasing
percentages of sulfur, and Compounds 3, 6, 7, and 8, the influence of the other
compounding ingredients.   The physical data on the compounds corre-
sponding to the smoked sheet pure-gum stock and to the one with the extender
are somewhat higher with reclaim. (compare Table 4, Compounds 7 and 6,
with Table 1, Compounds 1 and 2), but that is due mostly to the carbon black
content of the reclaim.   It might, however, be possible to make usable semi-
ebonite compounds from reclaim, if the desired physical data can be low.

SEMIEBONITES FROM HYCAR OR–25 AND GR–S COMPARED WITH THOSE FROM NATURAL RUBBER

GR-S and Hycar OR-25 compounds identical with those reported in Table 1
with natural rubber were tested, except that 15 parts of the unsaturated hydro-

TABLE 4

Compound No.	1	2	3	4	5	6	7	8
Whole-tire reclaim	200	200	200	200	200	200	200	200
Stearic acid	1	1	1	1	1	1	1	1
Sulfur	2	10	15	20	40	15	15	15
Zinc oxide	5	5	5	5	5	5	5	5
Naftolen R.100*	35	35	35	35	35	35	—	35
Suprex clay*	105	105	105	105	105	—	—	105
Pelletex*	—	—	—	—	—	—	—	105
Benzothiazoyl disulfide	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Diphenylguanidine	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Plasticity (compression in 0.001-in.)	145	110	95	95	110	255	135	95
Optimum cure at 80 lbs. (min.)	65	65	65	65	120	65	65	65
Shore hardness (30 sec.)								
Initial	50	73	76	80	84†	63	76	85
Aged 48 hrs. 100° C	62	82	89	94	84†	74	86	92
Tensile strength at break (lbs. per sq. in.)								
Initial	530	900	960	1250	2650	760	1060	1380
Aged 48 hrs. 100° C	610	990	570	810	2620	530	440	710
Elongation at break (%)								
Initial	330	190	130	120	1	140	140	70
Aged 48 hrs. 100° C	160	60	30	30	3	40	40	20

* The filler and the extender were incorporated in the form of premixed preparations containing 75% filler and 25% extender.

† D durometer reading.

carbon extender were used in the Hycar compound instead of 35 parts as with the other rubbers, and only 45 parts of filler, instead of 105 as with the other two rubbers.   (The amount of unsaturated hydrocarbon extender was reduced in the Hycar compounds to prevent bleeding out of the extender, since the grade used in this study is not compatible with butadiene-acrylonitrile rubbers in higher amounts.   The amount of filler was reduced since Hycar, inherently a stiffer rubber, does not require so high a filler content.)   In comparing the values given, this fact has to be kept in mind.

The test formulas are given in Table 5, and the results of the tests are shown in Figure 3.   It can be seen from the test formula in Table 5 that only the pure-gum stock of the Hycar compounds should be used for direct comparison with the other rubbers.   The four Hycar compounds are meant to be compared only in the group of Hycar compounds.   The bar graphs in Figure 3 show clearly the superiority of both GR-S and Hycar to natural rubber in the semiebonite range.   The influence of the unsaturated hydrocarbon extender, of the clay, and of the black on the properties graphed are also shown.   The solid bars in this figure represent the initial properties, the shaded bars, the properties of the aged compounds (48 hours at 100° C).
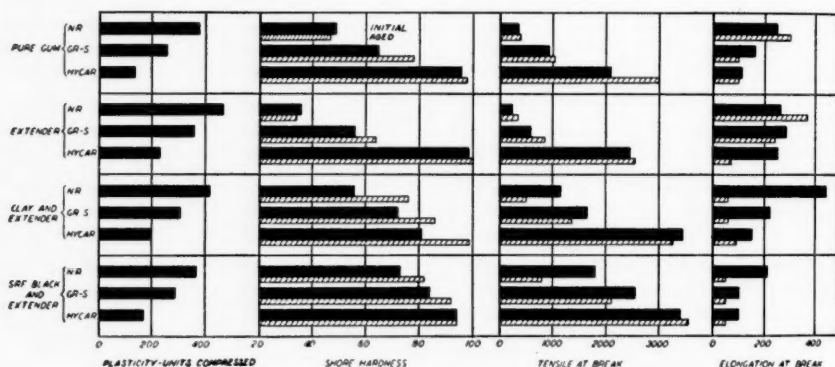
FIG. 3.—Comparison of natural rubber, GR-S, and Hycar semiebonites.

The first vertical column of bars shows the data for plasticity.   Each of the four sets of bars in this column shows the decrease of plasticity from natural rubber to Hycar.   The softening effect of the extender can be seen by comparing the first two sets of bars.   The influence of clay and SRF black on plasticity can be seen by comparing the bars in the second set with those in the third and fourth sets.   The second vertical column of bars presents the data for hardness; the third one, those for tensile; the last one, those for elongation.   The effect of any of the components on these properties can be seen by making the same comparisons as pointed out with the plasticity.

Table 3 presents data for a series of smoked-sheet compounds with increasing percentages of sulfur.   Figure 4 gives a comparison of the three rubbers as they respond to increase of sulfur when using the same series of test formulas, except that less extender and less clay were used with Hycar.   The solid lines are for the initial properties; the broken lines, for the aged properties.   The outstanding feature of this figure is the minima in the tensile curves for natural rubber, characterizing rather strikingly the semiebonite range as impractical.

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TABLE 5

Test formula	Natural rubber 100 smoked sheet				Butadiene-styrene rubber 100 GR-S				Butadiene-acrylonitrile rubber 100 Hycar OR-25			
	Pure gum	Extender	Extender and clay	Extender and SRF black	Pure gum	Extender	Extender and clay	Extender and SRF black	Pure gum	Extender	Extender and clay	Extender and SRF black
Rubber hydrocarbon												
Stearic acid	1				1				1			
Sulfur	15				15				15			
Zinc oxide	5				5				5			
Suprex clay	—	—	105	—	—	—	105	—	—	—	45	—
Pelletex	—	—	—	105	—	—	—	105	—	—	—	45
Naftolen R100	—	35	35	35	—	35	35	35	—	15	15	15
Benzothiazoyl disulfide	1.2				1.2				1.2			
Diphenylguanidine	0.2				0.2				0.2			
Optimum cure at 80 lbs. (min.)	65	35	65	35	65	65	80	65	120	120	90	90
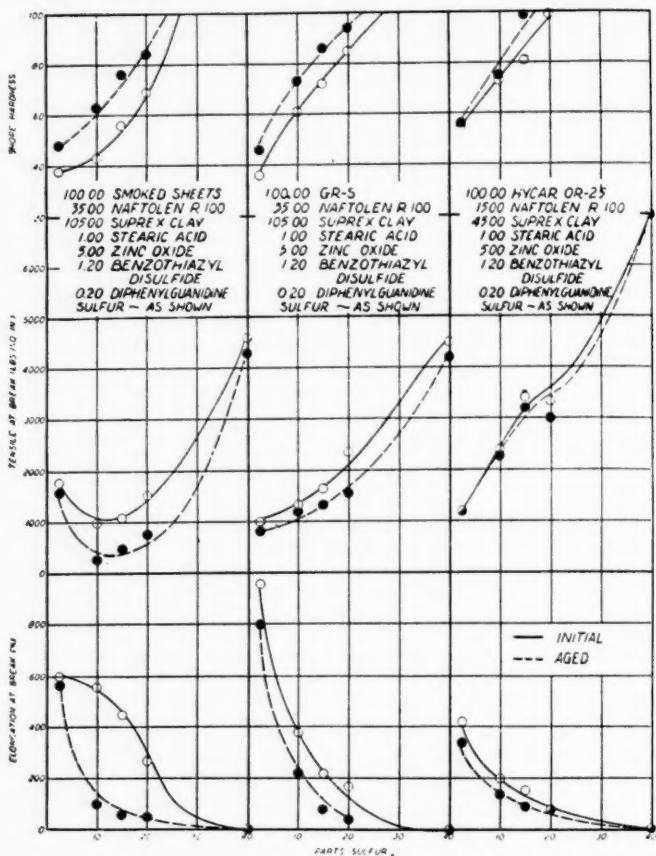
Fig. 4.—Effect of sulfur variation on natural rubber, GR-S, and Hycar.

No such minima appear in the curves for the other two rubbers, where the tensile strength increases gradually and similarly to the hardness, while the elongation decreases. (In comparing the data for the three rubbers it has to be kept in mind that the Hycar compounds contain only 15 parts of extender and 45 parts of clay, whereas the others contain 35 parts of extender and 105 of clay.)

FURTHER TESTS ON HYCAR

Table 6 reports a series of compounds based on Hycar OR-25 and SRF black. This series of compounds shows lower plasticity values than the compounds reported in Figure 4, owing to the reduced percentage of plasticizer and the use of SRF black instead of clay. The aging properties of the compounds are again good, as with previously shown Hycar compounds. The aging of these compounds was carried out in the Geer oven seven days at 70° C.

TABLE 6

Compound No.	1	2	3	4	5	6	7	8
Hycar OR-25	100	100	100	100	100	100	100	100
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulfur	2	5	10	15	20	30	35	40
Zinc oxide	5	5	5	5	5	5	5	5
Naftolen R100	10	10	10	10	10	10	10	10
Pelletex	75	75	75	75	75	75	75	75
Benzothiazoyl disulfide	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
Diphenylguanidine	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Plasticity (compression in 0.001-in.)	125	130	120	115	150	80	85	115
Optimum cure at 80 lbs. (min.)	50	60	60	60	60	60	60	60
Shore hardness (30 sec.)								
Initial	69	81	87	95	51*	89*	90*	88*
Aged 7 days Geer oven	69	84	90	97	77*	91*		
Tensile strength at break (lbs. per sq. in.)								
Initial	2830	3120	3260	3870	3650	7070	8240	8000
Aged 7 days Geer oven	2750	3450	3750	4300	3980	6480		
Elongation at break (%)								
Initial	360	200	120	70	70	5	4	3
Aged 7 days Geer oven	320	170	100	60	41	2		

* D durometer reading.

TABLE 7

Compound No.	1	2	3	4	5	6	7	8
GR-S	100	100	100	100	100	100	100	100
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulfur	3	5	10	15	20	25	30	40
Naftolen R100	35	35	35	35	35	35	35	35
Suprex clay	145	145	145	145	145	145	145	145
Zinc oxide	5	5	5	5	5	5	5	5
Benzothiazoyl disulfide	1.5	1.5	1.5	1.5	1.5	1.5	1.5	51.
Diphenylguanidine	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Plasticity (compression in 0.001-in.)	290	295	260	260	270	285	290	300
Optimum cure at 80 lbs. (min.)	60	60	60	60	120	120	120	120
Shore hardness (30 sec.)					A　D	A　D	D	D
Initial	44	51	69	76	84　35	94　47	77	87
Aged 7 days Geer oven	51	61	78	86	93　44	98　61	82	85
Tensile strength at break (lbs. per sq. in.)								
Initial	1125	1340	1380	1340	2040	2720	3120	5380
Aged 7 days Geer oven	950	970	1130	1670	2200	2750	2910	4500
Elongation at break (%)								
Initial	830	660	330	190	130	80	14	3
Aged 7 days Geer oven	760	530	240	130	70	40	3	2

TABLE 8

Compound No.	1	2	3	4	5	6	7	8
GR-S	100	100	100	100	100	100	100	100
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulfur	3	5	10	15	20	25	30	35
Zinc oxide	5	5	5	5	5	5	5	5
Naftolen R100	35	35	35	35	35	35	35	35
Pelletex	100	100	100	100	100	100	100	100
Benzothiazoyl disulfide	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Diphenylguanidine	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Plasticity (compression in 0.001-in.)	255	270	255	280	280	300	305	290
Optimum cure at 80 lbs. (min.)	60	60	60	90	90	120	90	120
Shore hardness (30 sec.)				A D	A D	A D	D	D
Initial	56	65	78	84 31	89 40	98 56	72	87
Aged 7 days Geer oven	59	67	81	87 33	91 40	99 63	74	86
Tensile strength at break (lbs. per sq. in.)								
Initial	1690	1810	2200	2520	3160	3550	3780	5410
Aged 7 days Geer oven	1730	1920	2210	2470	2900	3320	3150	5700
Elongation at break (%)								
Initial	400	230	140	110	100	38	29	4
Aged 7 days Geer oven	350	230	110	110	70	29	22	2

FURTHER TESTS ON GR–S

To check the suitability of GR-S for semiebonite in compounds of various compositions, the series reported in Tables 7–10 were mixed and tested. The data are presented again principally with the thought that this series might contain a suitable starting compound for further work.

Table 7 reports a series of compounds similar to those presented in Figure 4. However the compounds contain a higher percentage of clay, and the sulfur variation is in smaller increments. The gradual increase of hardness and tensile strength and the gradual decrease of elongation are clearly shown in this series. Aging is good through the whole sulfur range.

Table 8 reports a series of GR-S compounds containing 100 SRF black and 35 unsaturated hydrocarbon extender with increasing percentages of sulfur. Like the comparable series with clay, this series shows that GR-S gives usable compounds over the entire sulfur range.

Table 9 reports four compounds in the semiebonite range which contain again 100 SRF black, but only a small proportion of plasticizer. These four compounds are interesting to compare with Compounds 5 to 8 of the preceding series presented in Table 8. Consideration of the tensile strength and elongation figures shows that each of these compounds is most closely comparable with the one in the preceding series having five more parts of sulfur (1 of Table 9 to be compared with 5 of Table 8; 2 of Table 9 with 6 of Table 8; etc.). This is logical in view of the much higher total hydrocarbon content (rubber hydrocarbon plus extender hydrocarbon) of the series in Table 8. Comparison of the two series shows that the extender, although it has little effect on the physical properties of the vulcanizate, increases the plasticity considerably.

Table 10 shows the influence of increasing proportions of unsaturated hydrocarbon extender in GR-S semiebonites. In this series is seen the effect of increasing extender concentration at a constant sulfur level. Increasing the extender content provides a means of regulating the plasticity to any desired softness. The effect on the physical properties of the vulcanizate corresponds to a gradual decrease in sulfur concentration. This effect can be offset by increasing the sulfur to bring the physical properties back to the same level as

TABLE 9

Compound No.	1		2		3		4
GR-S	100		100		100		100
Stearic acid	0.5		0.5		0.5		0.5
Sulfur	15		20		25		30
Zinc oxide	5		5		5		5
Naftolen R100	5		5		5		5
Pelletex	100		100		100		100
Benzothiazoyl disulfide	1.2		1.2		1.2		1.2
Diphenylguanidine	0.2		0.2		0.2		0.2
Plasticity (compression in 0.001-in.)	125		125		125		120
Optimum cure at 80 lbs. (min.)	90		90		90		90
Shore hardness (30 sec.)	A	D	A	D	A	D	D
Initial	94	40	98	59	100	80	89
Aged 7 days Geer oven	95	52	99	67	100	82	90
Tensile strength break (lbs. per sq. in.)							
Initial	2600		3610		4450		6150
Aged 7 days Geer oven	2260		2840		3290		4790
Elongation at break (%)							
Initial	50		40		25		7
Aged 7 days Geer oven	40		40		11		2

TABLE 10

Compound No.	1	2	3	4	5
GR-S	100	100	100	100	100
Stearic acid	0.5	0.5	0.5	0.5	0.5
Sulfur	15	15	15	15	15
Zinc oxide	5	5	5	5	5
Magnesium oxide, extra light	10	10	10	10	10
Naftolen R100	—	10	20	35	50
Pelletex	100	100	100	100	100
Benzothiazoyl disulfide	1.2	1.2	1.2	1.2	1.2
Diphenylguanidine	0.25	0.25	0.25	0.25	0.25
Plasticity (compression in 0.001-in.)	90	120	185	265	315
Optimum cure at 80 lbs. (min.)	90	60	60	60	90
Shore hardness (30 sec.)					
Initial	98	96	94	90	86
Aged 48 hrs. 100° C	98	97	96	94	90
Tensile strength at break (lbs. per sq. in.)					
Initial	2870	3580	3410	2840	2480
Aged 48 hrs. 100° C	2930	3150	2970	2720	2490
Elongation at break (%)					
Initial	50	70	80	80	100
Aged 48 hrs. 100° C	30	50	60	60	70

the compound without extender.   Ten parts of magnesium oxide were used in addition to the zinc oxide in this series of compounds, since this addition was known to improve the aging characteristics of the compounds, possibly by activating the cure.   The physical properties are also somewhat higher, as can be seen by comparing Compound 4 of Table 10 with Compound 4 of Table 8.

SUMMARY AND CONCLUSIONS

To summarize the principal results of the present investigation, it was found that whereas natural rubber is a poor raw material for the manufacture of semiebonite, butadiene-styrene and butadiene-acrylonitrile rubbers are suitable raw materials, especially in combination with unsaturated hydrocarbon extenders of the Naftolen type.

The superiority of GR-S to natural rubber in the form of semiebonite should be an interesting piece of information for every compounder conscientious about the importance of keeping up the use and the manufacture of GR-S. With natural rubber becoming more and more available, there exists, as we all know, the definite danger that GR-S will be pushed into the background. As a matter of fact, we are approaching the situation where the supply of rubber hydrocarbons, natural and synthetic, will exceed the demand by multiples if new uses for rubber in large volume are not found.   The increased use of rubber products in the building and construction industry and in road surfacing might provide such an outlet for rubber.   Semiebonite with good aging qualities might find many uses along these lines.   It might lend itself to the manufacture of floor coverings, of waterproof wall insulation, etc.

The possibilities of using semiebonites from GR-S for tire beads has been suggested in a previously published article[4], but no detailed study comparing various rubbers has been reported.   The primary purpose of this report is to present these basic data, which can be used as starting points for compound development and to point out that we have in the semiebonite range a possibility of using GR-S to advantage.

As to butadiene-acrylonitrile rubbers, with which, in distinction to GR-S, very useful semihard rubber products can be made with phenolic resins, the

medium sulfur range opens the possibility of making semiebonites which are easier to process and cheaper than resin combinations. The use of plastics in the rubber industry was recently discussed and summarized by Winkelmann[5].

The compounding of semiebonites with Naftolen-type products offers a means of regulating the plasticity of the uncured stock as well as the elongation of the vulcanizate. Aging and prevention of sulfur bloom appear also improved. In other words, it was found that the combined use of 15 to 20 parts of sulfur with 15 to 50 parts of a Naftolen-type hydrocarbon gives a satisfactory semiebonite with GR-S, as well as with Hycar, and both these rubbers appear superior to natural rubber in semiebonites.

ACKNOWLEDGMENT

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STRAIN TEST FOR EVALUATION OF
RUBBER COMPOUNDS *

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The inherent variability of measurements for determining the stress-strain properties of vulcanized rubber is notorious. It has been customary to ascribe the cause of the variability entirely to the rubber. This allegation may be largely true in the case of stress and elongation at failure, but measurements by means of the strain test show that the measurements are responsible for a large portion of the observed variations of points on the stress-strain curve below failure.

Since the advent of the Government Synthetic Rubber Program in 1942, there has been an intensified effort to improve the precision of stress-strain testing. Measurements of the stress-temperature relations for pure-gum vulcanizates of GR-S and natural rubber by Roth and Wood[1] suggested that the precision and accuracy of stress-strain measurements might be greatly improved by measuring the elongations of rubber specimens suspending predetermined loads. Strain tests made in late 1944 on vulcanizates of X-125 GR-S and in 1945 on vulcanizates of natural rubber at the Institute Agronomico do Norte in Belem, Brazil[2], confirmed this suggestion. In the development of this test, strain measurements for the evaluation of vulcanized rubber have been found to yield information which has not been revealed by the usual stress-strain measurements.

PROCEDURE

In the strain test a predetermined load is applied to a specimen, and the elongation is measured after the load has been applied for a specified time. The load is selected to produce a specified force per unit of cross-sectional area of the unstretched specimen.

The early tests were performed with extremely simple equipment, which required manual application of the load to a standard dumbbell-shaped specimen having a reduced section two inches long. Most of the data reported here, however, were obtained by means of a tester developed by Holt, Knox, and Roth[3]. This tester is designed to minimize the number of manual operations and thereby to reduce the number of subjective errors. These authors also describe the preparation of the test-specimens and the measurement of their thickness, in addition to the measurement of strain at the specified stress. Strip specimens approximately $\frac{1}{4}$ inch wide and 6 inches long are used, since specimens with enlarged ends are not required for this test. These specimens can be cut from the standard 6 by 6 by 0.075 inch test sheet, and make it possible to increase the distance between bench marks to improve precision.

The bench marks are spaced 10 centimeters apart so that elongations can be read directly by means of a millimeter scale.

In early experiments a stress of 1000 lbs. per sq. in. was used for vulcanized specimens of GR-S and GR-I prepared according to the Specifications for Government Synthetic Rubbers[4]. In the course of development of the method the stress has been reduced in several steps to 400 lbs. per sq. in., which is employed at present for vulcanized tread-type compounds. The stress of 400 lbs. per sq. in. was selected because it is in the region where the ratio of elongation to stress attains a maximum value. A stress of 100 lbs. per sq. in. has been selected for gum vulcanizates of natural rubber and other rubbers to avoid effects of crystallization. The stress of 100 lbs. per sq. in. can also be used for studying gum vulcanizates of GR-S.
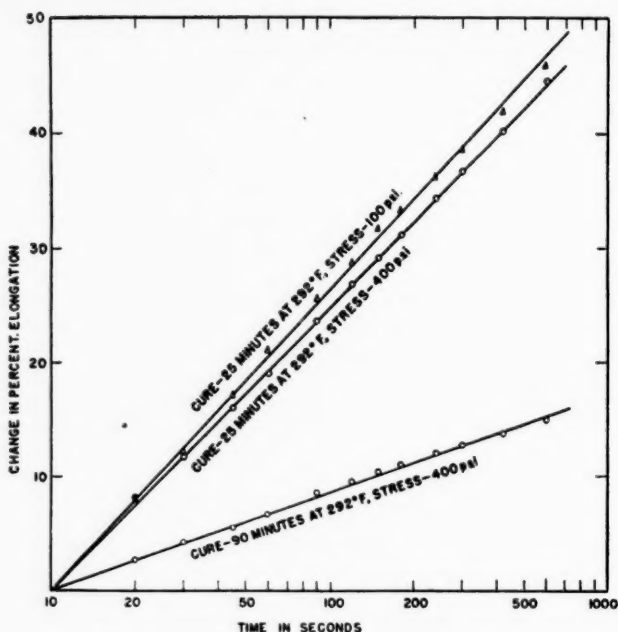
FIG. 1.—Creep of GR-S specimens under tensile stress.

The creep is shown as the difference between the elongation at any specified time and that at 10 seconds after application of the stress. The time scale is logarithmic.

For control testing and many research purposes, stresses of 100 to 400 lbs. per sq. in. are sufficient. Accordingly the tester developed by Holt, Knox, and Roth[3] is provided with weights for applying a stress of 100, 200, or 400 lbs. per sq. in. Stresses lower than 100 lbs. per sq. in. can be used provided the elongation is above 50 per cent. Minor modifications in the apparatus or procedure are necessary to measure lower elongations precisely. Stresses higher than 400 lbs. per sq. in. are obtained by suitable adjustment of the weights and are limited only by the strength of the specimen for the limiting extension of the specimen by the tester.

When the load is applied, the specimen elongates rapidly at first and then more slowly as time elapses. The precision of measurement increases as the

rate of creep decreases; hence observations can be made with greater precision as the time after application of the load increases. It is necessary, however, in a control test to keep the time for making a test at a minimum compatible with the requisite precision.

Measurements have been made at various intervals between 10 seconds and 10 minutes after application of the load. These measurements indicated that the elongation of the specimen increases approximately linearly with the logarithm of time. For example, in Figure 1, the increase in elongation after the 10-second reacing is plotted against the logarithm of time. The test-specimens were prepared from GR-S according to the Specifications for Government Synthetic Rubbers[4]. Vulcanizates cured 25 and 90 minutes at 292° F were employed. Specimens cured 25 minutes were tested with loads of both 100 and 400 lbs. per sq. in. to determine the effect of load. The specimens cured 90 minutes were tested only with a load of 400 lbs. per sq. in.

As can be seen in Figure 1, the rate of creep is approximately the same for the two loads; whereas the rate of creep for specimens cured 90 minutes is approximately one-third of that for those cured 25 minutes. None of the natural or other synthetic rubber vulcanizates investigated, including some without fillers, had a greater rate of creep than the GR-S carbon-black compound cured 25 minutes at 292° F. In those cases where crystallization occurred, the rate of creep was a maximum at intermediate loads. This phenomenon is in accordance with the observations for unvulcanized natural rubber by Treloar[5] and for vulcanized natural rubber by Field[6] and by Wildschut[7].

From a study of the data in Figure 1, in which the time is plotted on a logarithmic scale, a time interval of 60 seconds was selected for making subsequent measurements since observations made between 56 and 64 seconds are less in error due to creep than to errors in determining cross-sectional area of the specimen. With the automatic timing of the tester designed by Holt, Knox, and Roth[3], it is possible to retain the same precision with shorter time intervals by reducing the period permitted for observation by a proportionate amount; that is, measurements made between 28 and 32 seconds are as precise as those made between 56 and 64 seconds. The absolute value of the elongation, however, is lower at 30 seconds than at 60 seconds, as is indicated in Figure 1.

PRECISION OF TEST

The high precision of the strain test is achieved largely by measuring the elongation under nearly static conditions instead of taking observations as the specimen is being extended. This precision can be seen in Table 1, which gives the standard deviations among specimens from the same sheet of vulcanized rubber. The values represent data obtained during the evaluation of reference lots of Government Synthetic Rubbers. With the exception of the values for X-125 GR-S, which were obtained with two-inch dumbbell specimens and manually applied loads, the standard deviations are essentially identical for all rubbers tested during the past three years, and are comparatively small. Since these values are in units of elongation, they cannot be compared directly with those for tensile stress. A comparison can be made, however, by converting one into the units of the other. In Table 2 the standard deviations for strain are converted into equivalent stress values and compared with those for tensile stress as follows.

1. Six sheets from the same compounded batch of X-243 GR-S were cured for each of the times indicated; three sheets of each cure were used for measurements of tensile stress and three for those of strain.

TABLE 1

PRECISION OF STRAIN MEASUREMENTS

Type of rubber	Date of tests	Number of sheets tested	Stress (lbs. per sq. in.)	Standard deviations of strain for specimens within a sheet (percentage)		
				25 min.†	50 min.†	90 min†.
*GR-S X-125	December 1944	2	1000	7.5	5.9	4.3
X-179	February 1945	22	1000	2.8	2.5	1.4
X-224	July 1945	9	1000	4.9	2.4	1.7
X-224	July 1945	9	1000	3.8	2.2	1.9
X-224	July 1945	9	1000	2.6	2.0	1.9
X-243	December 1945	20	1000	3.3	1.7	1.8
X-224	April 1946	12	750	1.5	3.1	1.8
X-289	April 1946	12	750	2.0	3.2	1.2
X-289	January 1947	11	600	3.0	1.1	0.9
X-346	January 1947	21	600	3.0	1.5	0.8
X-346	July 1947	20	600	2.6	2.2	1.4
X-387	July 1947	40	600	3.1	2.0	1.4
X-387	December 1947	16	600	3.2	1.5	1.8
X-418	December 1947	36	600	3.5	2.1	1.3
X-412	December 1947	30	600	3.8	1.5	2.8
X-418	February 1948	54	400	2.5	1.2	‡0.7
				20 min.§	40 min.§	80 min.§
GR-I Y-100	April 1945	20	1000	3.3	2.9	2.3
Y-102	January 1947	8	600	1.7	1.5	1.3
Y-103	January 1947	16	600	1.6	1.1	1.2
				10 min.†	10 min.§	20 min.§
GR-M (10 lots)	July 1946	20	600	3.1	2.5	2.2

* Used two-inch dumbbell-shaped specimens and applied load manually.
† Time of cure at 292° F.
‡ Cured 100 minutes at 292° F.
§ Time of cure at 307° F.

TABLE 2

COMPARISON OF PRECISION OF STRAIN TEST WITH PRECISION OF USUAL TENSILE STRESS TEST

			Compounds of X-243 GR-S vulcanized					
			25′ at 292° F		50′ at 292° F		90′ at 292° F	
Line	Test	Statistics	Stress P.S.I.	Strain %	Stress P.S.I.	Strain %	Stress P.S.I.	Strain %
1	Stress	Mean	407	300	1089	300	1543	300
2	Strain	Mean	350	298.9	1050	324.7	1500	330.1
3	Strain	Mean	400	328.9	1100	335.2	1550	338.2
4	Strain	Mean	450	355.3	1150	344.8	1600	348.8
5	Stress	S. D.*	18.8	..	30.2	..	45.2	..
6	Strain	S. D.*	..	4.36	..	3.26	..	2.74
7	Strain	$\Delta E/\Delta S$†	..	0.564	..	0.201	..	0.187
8	Strain	S. D.‡	7.72	..	16.2	..	14.7	..
9		Ratio§	2.44	..	1.86	..	3.07	..

* Standard deviation of specimens within a sheet.
† The change in elongation for a change in stress of one lb. per sq. in. (line 4 minus line 2)/100.
‡ Standard deviation of strain measurements expressed in equivalent stress units, which is calculated by dividing the strain standard deviation by $\Delta E/\Delta S$, line 6/line 7.
§ Ratio of standard deviation for tensile stress to that for strain both expressed in lbs. per sq. in., line 5/line 8.

2. The tensile stress at 300 per cent elongation was measured on 6 specimens from each of the three sheets; the elongation was measured on 18 specimens from each sheet, 6 at a stress approximately equivalent to the average tensile stress at 300 per cent elongation, 6 at a stress 50 lbs. per sq. in. lower, and 6 at a stress 50 lbs. per sq. in. higher.   The mean values for each of these properties are shown in the first four lines of Table 2.

3. The standard deviations among specimens were calculated for tensile stress and for strain measurements, and are given in lines 5 and 6 of Table 2. The change in elongation produced by a change in stress of one lb. per sq. in. was calculated from the strain measurements in lines 2 to 4, and is shown in line 7.   The values of the standard deviations in line 6 were divided by the corresponding values in line 7 to obtain the equivalent standard deviations in units of stress shown in line 8.

4. The ratios of the values in line 5 to those in line 8, given in the last line, indicate that the standard deviations for tensile stress measurements at 300

TABLE 3

VARIANCES OF STRESS AND STRAIN MEASUREMENTS

Type of GR-S	Minutes cure at 292° F	Variances			
		A Batch means* Stress at 300%	B Specimens† elongation (lbs. per sq. in.)²	C B/5	D C/A %
X-346	25	509	1320	264	52
	50	824	1297	259	31
	90	708	1801	360	51
X-289	25	133	276	55	41
	50	658	931	186	28
	90	1847	1120	224	12
		%²	Strain at 600 lbs. per sq. in. %²	%²	%
X-346	25	78.9	9.00	1.80	2.3
	50	24.6	2.16	0.43	1.8
	90	1.8	0.65	0.13	7.2
X-289	25	56.0	8.86	1.77	3.2
	50	5.3	1.12	0.22	4.2
	90	8.9	0.73	0.15	1.7

* Variances apply to 27 batches of X-346 GR-S and 11 batches of X-289 GR-S.
† Variances apply to five specimens from a sheet from each batch, *i.e.*, a total of 135 specimens of X-346 and 55 specimens of X-289 GR-S.

per cent elongation are approximately $2\frac{1}{2}$ times as large as the equivalent values for strain measurements.

Another comparison of the precision of measurements made by these two methods of test is possible by subjecting the data obtained on reference lots of synthetic rubbers to an analysis of variance[8].   Such an analysis for X-289 and X-346 GR-S is given in Table 3.   Column A lists for each property the variances (squares of standard deviations) among batch means, and Column B lists the variances among specimens from the same batch.   The values in Column A may be resolved into two components, one due to variations from batch to batch, the other to variations among specimens from the same batch.   Since five specimens from each batch were tested, the contributions from variations among specimens to the variances in Column A are $\frac{1}{5}$ of the variances in Column

TABLE 4

TYPICAL DATA FOR STRAIN AND SET OF INDIVIDUAL SPECIMENS

Date 1946	Strain at 600 lbs. per sq. in. (%)			Set † (%)		
	25 min.*	50 min.*	90 min.*	25 min.*	50 min.*	90 min.*
Oct. 22	450	245	190	10.5	4.5	3.0
	450	245	190	10.5	4.5	3.0
	452	242	192	10.5	4.6	3.2
	456	245	191	10.6	4.3	3.0
	457	245	191	10.6	4.5	3.2
Av.	453	244	191	10.5	4.5	3.1
Oct. 23	492	256	190	10.5	4.8	3.2
	485	256	190	10.8	4.8	3.4
	484	256	192	10.7	4.8	3.3
	488	255	190	10.7	5.0	3.3
	485	257	190	10.7	5.0	3.3
Av.	487	256	190	10.7	4.9	3.3
Oct. 24	486	248	193	13.4	5.0	3.0
	484	250	194	13.4	5.0	3.0
	481	250	194	13.4	4.9	3.5
	485	250	192	13.6	4.9	3.5
	485	249	193	13.6	5.0	3.5
Av.	484	249	193	13.5	5.0	3.3
Oct. 29	446	244	190	12.0	4.4	3.8
	446	241	190	12.3	4.4	3.8
	445	243	190	12.3	4.2	3.6
	448	242	190	12.4	4.3	3.7
	446	240	190	12.3	4.3	3.6
Av.	446	242	190	12.3	4.3	3.7
Oct. 30	486	252	193	13.5	5.0	3.4
	486	252	191	13.5	5.0	3.5
	486	250	190	13.2	5.0	3.5
	485	249	189	13.5	5.0	3.4
	487	247	188	13.4	4.9	3.5
Av.	486	250	190	13.4	5.0	3.5

* Time of cure at 292° F X-289 GR-S vulcanizates prepared according to the Specifications for Government Synthetic Rubbers, effective January 1, 1946.
† Set measurements made one hour after strain measurements on same specimens.

B and are listed in Column C. Column D expresses this contribution as a percentage of the observed variance among the batch means. In the case of elongation at 600 lbs. per sq. in., testing variations account for approximately 3.4 per cent of the observed batch-to-batch variations, which is about one-tenth the corresponding percentage for stress at 300 per cent elongation. Similar results have been obtained in the evaluation of Y-102 and Y-103 GR-I. Other laboratories[9] have noted comparable improvements in precision of testing by means of the strain test.

APPLICATIONS OF STRAIN TEST

The high precision of the strain test has made it possible to obtain a reliable evaluation of vulcanized rubber samples by means of relatively few measure-

ments. For example, it has been possible to determine with little effort the variations introduced during compounding and curing, the heterogeneity of a single sheet of rubber, and the change in stress-strain properties during storage of vulcanized rubber.

In Table 3 the large variance among batch means compared to the variance among specimens for the strain data indicates that there was considerable variability in the compounding and curing operations. Similar data are shown in Table 4, where values for individual specimens from five batches prepared on different days are given. The agreement among the specimens from a single sheet from each batch is excellent, but the batch averages vary considerably. To determine whether this variation is related to the compounding or curing procedure, six sheets from the same batch were vulcanized simultaneously. The average value for each of the six sheets is given in Table 5. The variation among sheets cured from the same batch is considerably more than expected from specimen variations, and is an appreciable fraction of the variation among batches noted in Table 4. From an analysis of variance[8] made on data, not reported here, for approximately 100 pairs of sheets of X-412 and X-418 GR-S

TABLE 5

STRAIN AND SET DATA FOR SHEETS WITHIN A BATCH
OF X-289 GR-S VULCANIZATES

	Strain at 600 lbs. per sq. in. (%)			Set † (%)		
Sheet	25 min.*	50 min.*	90 min.*	25 min.*	50 min.*	90 min.*
1	471	254.6	194.3	12.15	4.50	3.23
2	484	255.7	193.7	‡14.85	4.74	3.16
3	468	251.2	192.9	‡12.66	4.54	3.15
4	498	258.0	191.5	‡14.07	4.91	3.36
5	465	253.0	192.9	‡12.70	4.68	3.36
6	468	253.6	191.9	12.48	..	3.23‡
Av.	476	254.5	192.9	13.15	4.67	3.25

* Time of cure at 292° F.
† Set measurements were made one hour after strain measurements on same specimens.
‡ Mean for six specimens; other values are means for twenty specimens.

vulcanizates, it was inferred that the true variance among batches is approximately two times the true variance among sheets within a batch.

In addition to its use for detecting compounding and curing variables, the strain test is sufficiently sensitive to detect variations within a single sheet of vulcanized rubber. The narrow specimen used in this test makes it possible to cut 20 specimens from a sheet six inches square. The variations among 20 such specimens are seen in Figure 2. The figure shows the individual strain values for the sheets vulcanized 25 and 90 minutes, respectively, which are summarized in Table 5. The elongation of each specimen is plotted in the order of its position in the sheet. The trends in values noted across most sheets are believed to be due to grain effects caused by flow during the early part of vulcanization. This conclusion is supported by the studies of Gurney and Gough[10].

Since 20 specimens can be cut from a single sheet, it is possible to study the change in stress-strain properties of vulcanized rubber during storage. Figure 3 shows the average change in five sheets of each of three GR-S vulcanizates during the first six days of storage at 82° F. These data show the
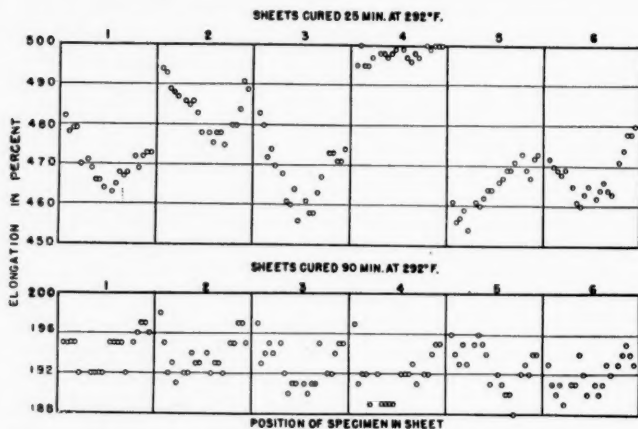
FIG. 2.—Heterogeneity within and among sheets from same compounded batch. The mean value for each sheet and the conditions of test are given in Table 5.
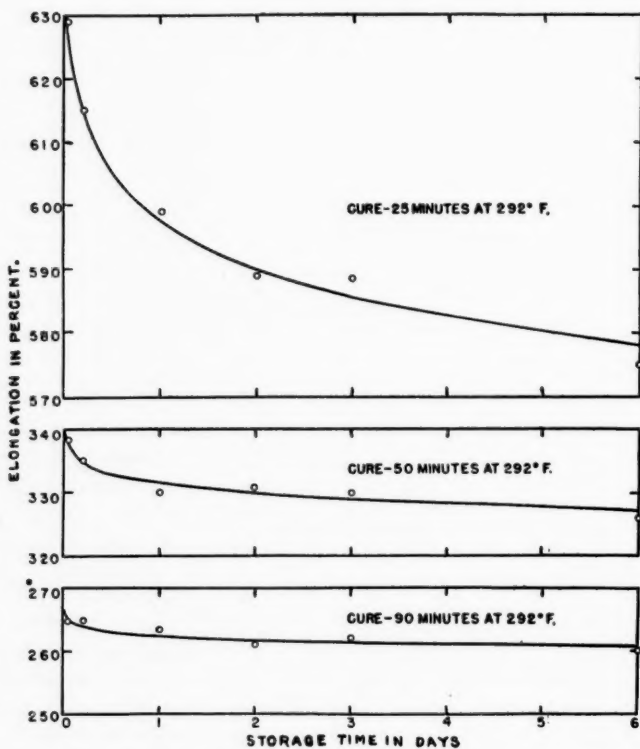
FIG. 3.—Effect of storage at 82° F on elongation at 600 lbs. per sq. in. for vulcanizates of X-243 GR-S.

marked stiffening of undercured rubber during the first 24 hours after vulcanization, and support the minimum aging period of 24 hours between vulcanization and testing required by A.S.T.M. Method D15–41 and of 16 hours by the Specifications for Government Synthetic Rubbers. It should be emphasized that the strain test made it possible to obtain these results from only one batch for each cure.

METHOD FOR MEASURING SET

Specimens subjected to the strain test can be conveniently used for precise measurement of extension set for a specified stress, since the specimens are subjected to a uniform stress for a uniform period of time. Such measurements of set after the specimens have been allowed to recover for one hour are presented in Table 4. As seen in this table, the dispersion of values for specimens from the same sheet is remarkably small, so it is easy to detect variations among sheets or batches. The results of set measurements shown in Table 5 indicate that there is an appreciable variation in set among sheets from the same batch, although not so large as that among batches shown in Table 4.

DETERMINATION OF VULCANIZATION PARAMETERS

In the usual measurements of tensile stress (modulus) of rubbers vulcanized for different periods of time, considerable ambiguity arises in differentiating between cure characteristics and the inherent stiffness of the rubber compound. An examination of strain data plotted as a function of time of cure, as in Figure 4, indicates that the curve is a rectangular hyperbola of the form $(E - a)$ $(t - b) = c$, where E is the elongation at time of cure t. On differentiation, this equation becomes: $-dE/dt = (E - b)^2/C$. This equation suggests that elongation at a fixed stress decreases with time of cure according to the laws of a second-order reaction, in which the reaction rate constant (k) is $1/C$. The parameter b is independent of the time of cure and corresponds to the elongation (E^∞) for infinite cure time. The parameter a is the constant of integration, and corresponds to the time (t_0) at which the elongation begins to decrease. This time may be considered as the point of incipient cure or scorch time. Thus strain data may be useful for determining three parameters of vulcanization: (1) scorch time, t_0; (2) reaction rate constant, k; and (3) a structure factor, E^∞, which may be associated with the inherent stiffness of the rubber compound. This stiffness may be due to the structure of the polymer or the nature and concentration of the compounding ingredients. As seen in Figure 4, E^∞ is a function of the applied stress; whereas t_0 is independent of it. The reaction rate constant, k, is also a function of the applied stress which must be considered in comparing compounds with different stress-strain characteristics.

This relation has been found to apply to vulcanized GR-S, GR-M, and natural rubber compounds. In the case of rubbers which crystallize on stretching, however, t_0 decreases and may become negative as crystallization increases. Accordingly, if t_0 is to be regarded as a scorch time, the stress should be sufficiently low to avoid crystallization. Reversion is another phenomenon which affects the vulcanization parameters. When reversion occurs, E reaches a minimum and then increases instead of approaching an asymptote as the cure time increases indefinitely. Further, the parameters are extremely sensitive to the observed variations between sheets noted in Table 5. It is, therefore, essential to use the average value from several sheets to obtain reliable values
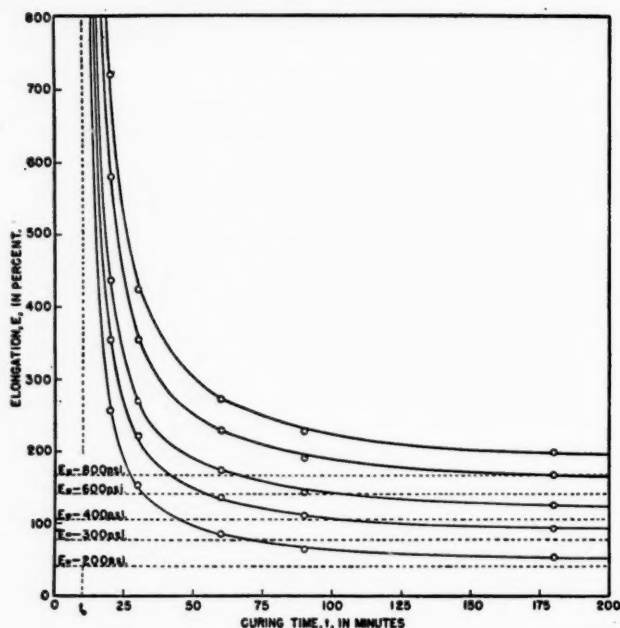
FIG. 4.—Elongations for various stresses *vs.* time of vulcanization of X-387 GR-S at 292° F.

The solid lines are hyperbolas calculated from the equation, $(t - t_0)(E - E_\infty) k = 1$, using the following values for the parameters:

Stress P.S.I.	t Min.	E^∞ %	k (Min. $\times$ %)$^{-1}$
200	11	41	0.000488
300	11	78	.000392
400	11	107	.000329
600	11	142	.000250
800	11	168	.000203

for the parameters. Employing the average values obtained in the evaluation of X-289, X-346, and X-387 GR-S, the constants given in Table 6 were calculated for the vulcanization parameters, t_0, k, and E^∞.

SUMMARY AND CONCLUSIONS

Measurements of elongation of rubber vulcanizates at a fixed stress have been made with a precision much greater than can be obtained in the usual measurements of stress at a specified elongation. Such measurements form the

TABLE 6

VULCANIZATION PARAMETERS DERIVED FROM STRAIN DATA

Type of GR-S	Date tested	Scorch time t_0 min.	Reaction rate constant, k (Min. $\times$ %)$^{-1}$	Structure factor E at 600 lbs. per sq. in. %
X-289	Oct., 1946	13.0	0.000249	138
X-289	Jan., 1947	12.1	0.000239	138
X-346	Jan., 1947	10.9	0.000265	135
X-346	July, 1947	11.0	0.000247	130
X-387	July, 1947	11.0	0.000234	136

basis of a strain test developed to characterize rubber vulcanizates in control and research testing. Statistical analyses show that the errors introduced in the actual strain measurements are negligible compared to those introduced by variations during compounding and curing, whereas the errors introduced by the usual measurements of stress at a specified elongation are of the same order of magnitude as those for compounding and curing. The high precision of strain testing has been used to detect variations within a single sheet of vulcanized rubber and variations among sheets cured from the same compounded batch. It has been possible also to determine with a single sheet its change in stiffness or modulus with age. The uniform treatment of specimens in the strain test makes them particularly useful for precise measurements of set. Further, it has been found that the decrease in elongation with time of cure apparently follows the laws of a second-order chemical reaction; consequently it is possible to represent the data by an equation involving three vulcanization parameters.

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STRAIN TESTER FOR RUBBER *

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The strain tester described herein[1] was designed to measure strain at a definite time after the application of a predetermined stress. In the usual testing procedure, stress is measured at a specified strain during extension of the specimen at a relatively rapid rate. Interest in the development of the strain tester resulted from investigations by one of us[2], which showed that replicate measurements of strain at a predetermined stress have a variance of approximately one-tenth the variance of the usual measurements of stress at a specified strain.

The apparatus was designed to make possible routine measurements of strain at any selected stress below rupture with the degree of precision found by Roth in the earlier investigation. In designing the strain tester, accuracy of measurement, as well as precision, was considered. The design features which are responsible for the improved precision and accuracy of measurements in the strain test are: (1) observation of bench marks when they are essentially at rest, (2) use of freely suspended weights to attain the desired stresses without friction effects, and (3) increase in distance between bench marks of from two to four times that possible with usual dumbbell-shaped specimens.

This test is not intended to measure stress-strain properties near or at rupture. For control testing, however, and for many research tests a knowledge of the properties below the region of failure is sufficient. The improved precision of the strain test warrants a separate determination of the properties at failure when necessary.

DETAILS OF CONSTRUCTION

Three accessory instruments are required to prepare specimens for measurements in the strain tester: (1) a die to cut specimens from a sheet of rubber; (2) a device for placing bench marks on the specimen; and (3) a device for determining the average thickness of the specimen. The construction of each of these instruments and of the strain tester is described in turn.

DIE FOR CUTTING SPECIMEN

The construction of the die used to cut specimens from a sheet of rubber is shown in Figure 1. The cutting blades of the die consist of six strips of razor-blade steel sharpened on one edge. Each strip is six inches long, $\frac{3}{4}$-inch wide, and 0.009-inch thick[3]. They are clamped between metal spacers six inches long, $\frac{5}{8}$ inch wide, and 0.245 inch thick, so that the cutting edges project $\frac{1}{8}$ inch. The die is used in an arbor press or clicking machine.

With this device five strips 0.254 inch in width are cut simultaneously. This width was chosen for its convenience in determining the load to be applied to the specimen to obtain the desired stress based on the cross-sectional area
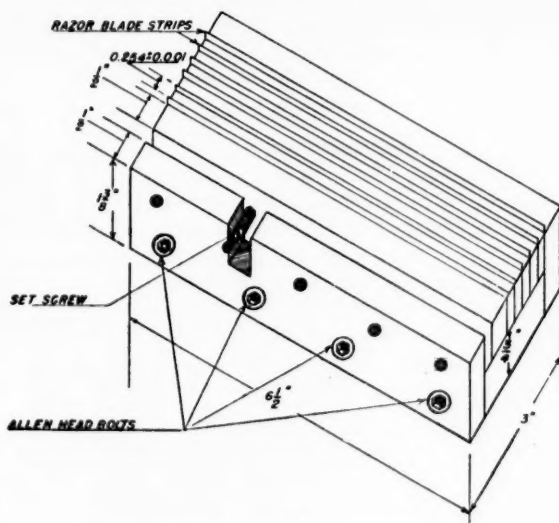
FIG. 1.—Die for cutting five test-specimens.

of the unstrained specimen.   The width is one-hundredth the numerical factor
by which the thickness in millimeters must be divided to convert it to inches.
Consequently the load, expressed in pounds, is equal to the numerical value of
the thickness of the specimen measured in millimeters multiplied by the
numerical value of the desired stress expressed in hundredweights per square
inch.   For example, to obtain a stress of 400 lbs. per sq. in., the load to be ap-
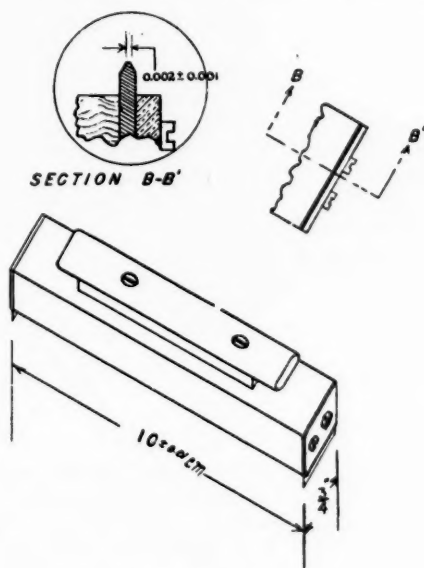
FIG. 2.—Bench marker.

plied to a specimen 2.03 millimeters thick and 0.254 inch wide would be: 2.03 × 400/100 = 8.12 pounds.

BENCH MARKER

Bench marks are placed 10 centimeters apart on each specimen. This distance makes it convenient to measure elongation (strain) directly by means of a scale graduated in millimeters. The device used is essentially a metal bar with razor blades fastened on each end, as shown in Figure 2. To prevent cutting of the specimen by the blade, the edges are ground as shown in the detailed section. With this marker, distinct lines not over 0.010 inch wide are easily made.
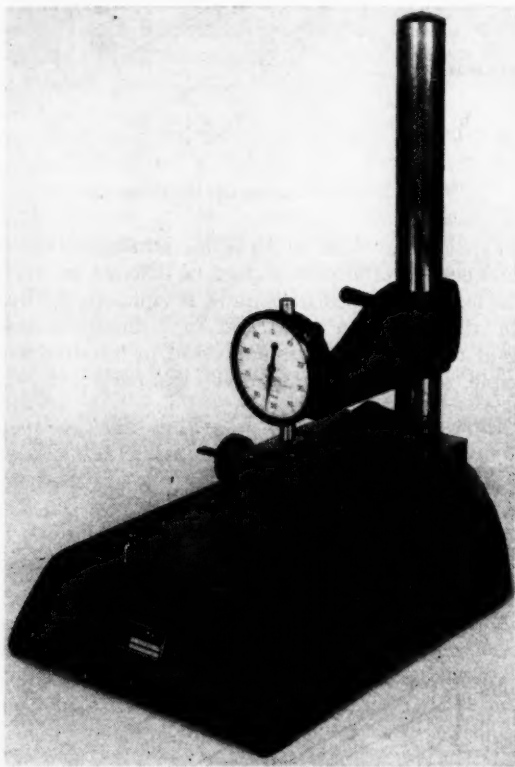
FIG. 3.—Gage for obtaining average thickness of the specimen.

THICKNESS GAGE

The thickness of the specimens is measured with the gage shown in Figure 3. This gage has a dial indicator graduated in hundredths of a millimeter. One revolution of the pointer corresponds to 1.0 millimeter, and the total range of the indicator is 2.5 millimeters. The indicator is mounted above an especially constructed base shown in Figure 4. An important feature of this base is

the pressure bar arrangement. This metal bar, 10 centimeters long, is pressed
on the surface of the specimen with a force of four pounds by means of a spring.
The bar is attached to a ball joint which possesses sufficient freedom of move-
ment to average the thickness of wedge-shaped specimens. The dial indicator
is adjusted to read zero for specimens 1.50 millimeters thick, since specimens
of this thickness require a load corresponding to the basic weight of the weight
assembly described below under "Strain Tester". Additional thickness beyond
1.50 millimeters is read in hundredths of a millimeter.

STRAIN TESTER

The strain tester is designed to apply automatically the selected weights to a
specimen to produce the desired stress, to provide means for measuring the
elongation accurately and easily, to assure that measurement of elongation is
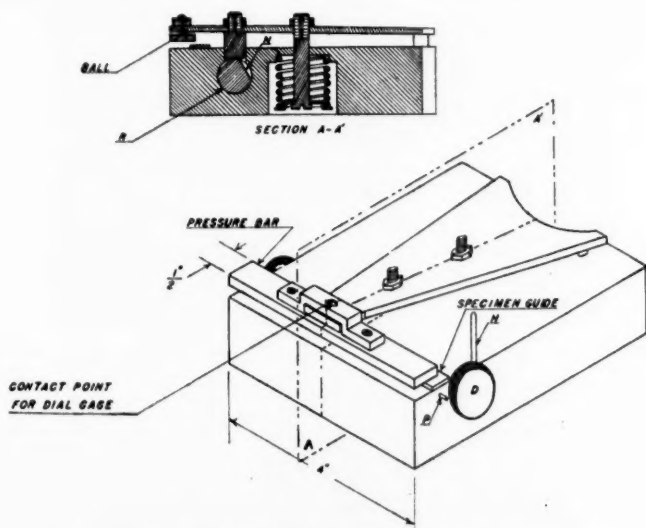
FIG. 4.—Construction of the averaging mechanism of the thickness gage.

The apparatus is shown with the pressure bar raised. The specimen is placed on the base under the
bar and against the guide. When the knurled disk, *D*, is turned so that the handle, *H*, rests against the
pin, *P*, the notch, *N*, in the rod, *R*, is at the top, allowing the spring to pull the pressure bar down against
the top side of the specimen.

made at the proper time after application of the load, and to return automati-
cally the specimen and the tester to their starting positions after the measure-
ment has been made. The design of the tester embodies mechanical and
electrical features which are discussed separately.

MECHANICAL ASSEMBLY

Figures 5 and 6 are photographs of the strain tester. Essentially the tester
consists of two parts. The upper part comprises a vertical track, the driving
mechanism for extending and suspending the specimen, and the mechanism
for measuring the elongation. The lower part consists of the weight assembly
and mechanism for placing the proper load on the specimen.

The vertical track is constructed from five strips of cold rolled steel 48 inches long.   The basic steel strip is two inches in width and $\frac{3}{8}$ inch thick. To this strip two strips $\frac{5}{8}$ by $\frac{1}{8}$ inch and two strips $\frac{3}{4}$ by $\frac{1}{8}$ inch are fastened to form a T-slot $\frac{3}{4}$ inch wide at the base and $\frac{1}{2}$ inch at the throat.   This slot serves as a guide for the grip which stretches and supports the upper end of the specimen.   The specimen grip also connects the two ends of a roller chain[4] which passes over sprockets at each end of the vertical track and thence to a $\frac{1}{8}$ or $\frac{1}{4}$ h.p. gear motor.   This motor raises and lowers the specimen grip in the T-slot
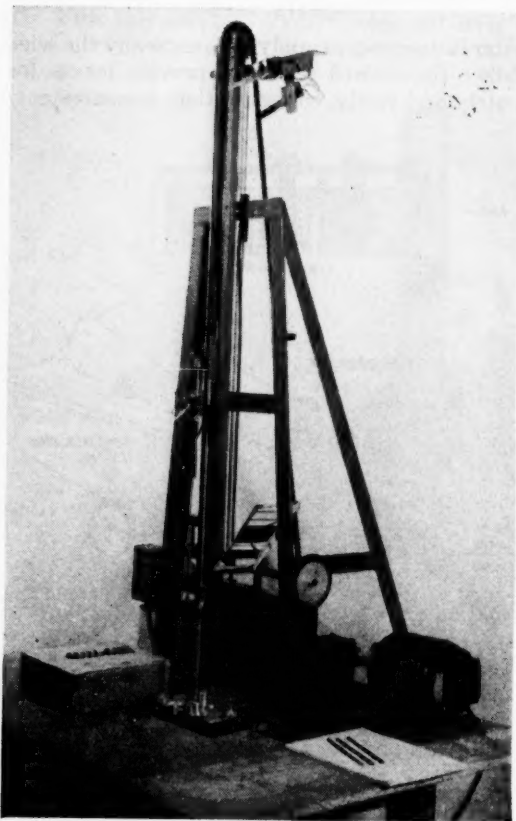
Fig. 5.—General view of rubber strain tester.

at a speed of 200 inches a minute.   Two limit switches located fore and aft of the sprocket at the upper end of the track prevent the specimen grip from reaching the sprockets and damaging the tester.

A steel tape graduated in millimeters is used to measure the elongation. Since the bench marks are placed on the specimen 10 centimeters apart, each millimeter of extension corresponds to an elongation of 1 per cent.   Two transparent plastic positioners with hair lines are used to locate the position of the bench marks on the millimeter tape.   The end of the tape is fixed to the upper positioner, and the zero point on the tape is adjusted exactly 10 centi-
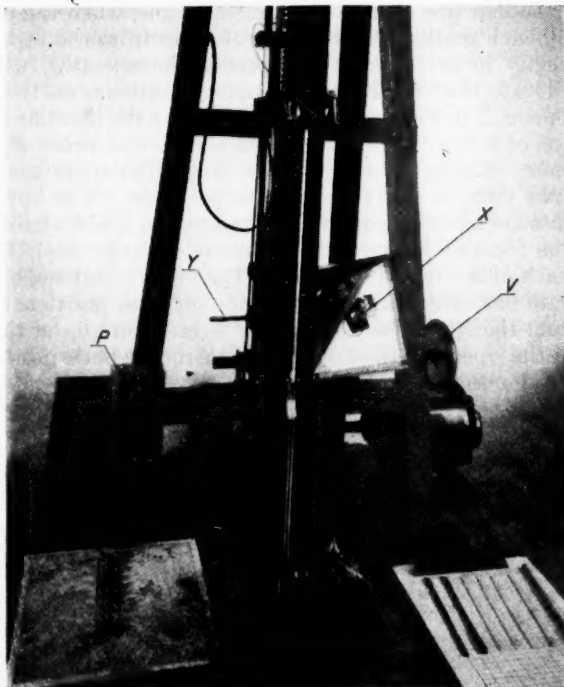
Fig. 6.—Rubber strain tester from the perspective of the operator.

P, pilot in series with motor of time-cycle controller.
V, hand-wheel for aligning upper positioner with upper bench mark.
X, prism and specimen as seen in plane mirror.
Y, handle for rotating positioners to the specimen and aligning the lower positioner with the lower bench mark.
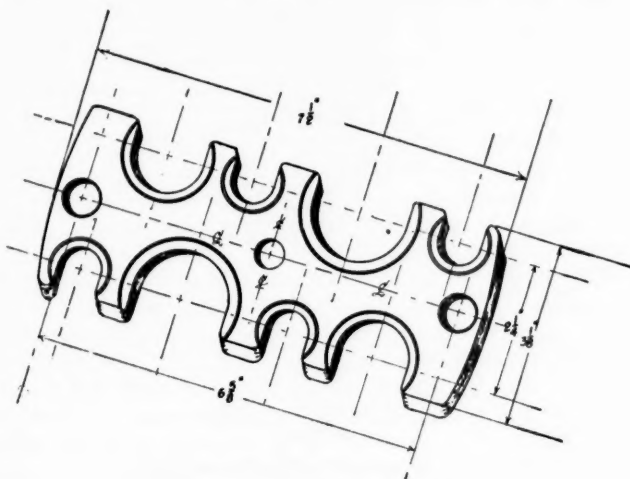
Fig. 7.—Holder for additive weights.

meters below the hair line on this positioner. Thus, when the positioners are placed on the bench marks, the elongation is read from the tape at the lower positioner directly in percentage. To permit the operator, when seated at the tester, to locate the hair line of the upper positioner on the upper bench mark, arrangement X in Figure 6 is made to observe the hair line and the bench mark by means of a fixed plane mirror and a reflecting prism attached to the upper positioner. Lights attached to the prism illuminate the upper bench mark during the time an observation is to be made. The upper positioner, prism, and lights are moved up or down by means of a ladder chain and sprocket assembly. The asembly is driven by means of a hand-wheel, V in Figure 6, within easy reach of the seated operator. The lower positioner slides freely on a vertical square bar, which serves as a guide for both positioners and rotates them away from the specimen. A handle, Y in Figure 6, on the lower positioner enables the operator to slide it and to rotate both positioners to the specimen to make observations without parallax.
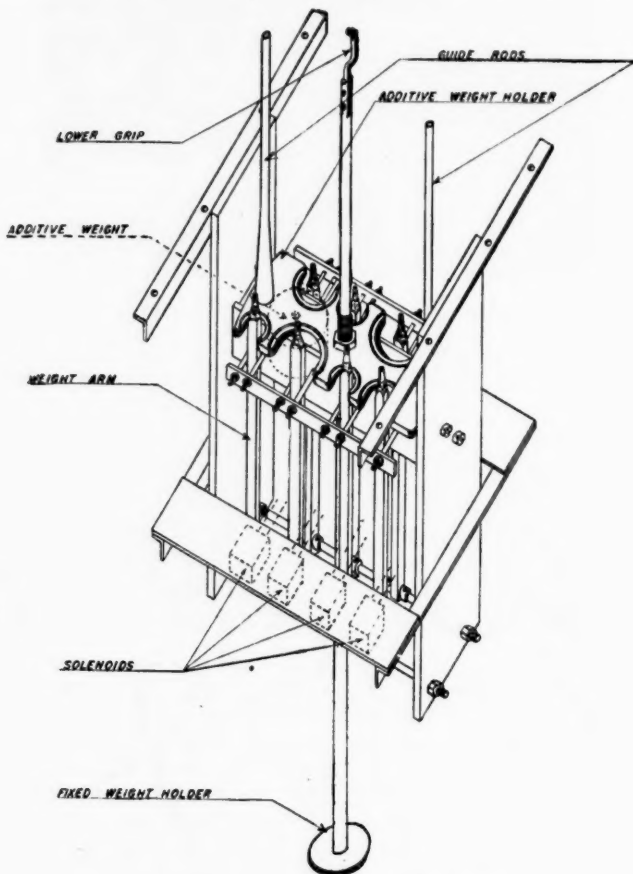
FIG. 8.—Weight assembly and loading mechanism.

The weight arms are shown in their vertical position. In operation there are never more than four arms in this position at one time. One of the additive weights is shown by dashed lines in position on the weight arm.

The lower part of the apparatus, consisting of the weight assembly and weight loading mechanism, is centered around a plumb line from the upper grip. The weight assembly passes freely through a rectangular hole five by eight inches cut in the table top which supports the upper and the lower parts of the apparatus. The assembly consists of an aluminum rod (approximately 32 inches long) on which are fastened two weight holders, one at the lower end for the fixed weight and the other about 24 inches above for the additive weights. At the upper end of the rod is fastened the grip for the lower end of the speci- men. The holder for the additive weights is constructed as shown in Figure 7. Guide rods pass through the holes in the ends of the weight-holder, and the additive weights are placed in the semi-circular notches on the sides.

The combination of the weight asembly and weight loading mechanism is shown in Figure 8. The eight additive weights are supported on arms nor- mally inclined at an angle of about eight degrees from the vertical. When additive weights are needed, the arms supporting the selected weights are moved to a vertical position. The additive weights are then lifted from the ends of the arms by the upward movement of the weight holder at the time the specimen is elongated. The weights are returned to the arms during the retraction of the specimen.

The arms are moved to the vertical position by means of solenoids and returned to their normal position by the action of a coil spring after the circuit to the solenoid is broken. The mechanism for actuating the solenoids and the mechanism for indicating when the weight assembly is suspended freely are discussed in the section on the electrical circuit.

ELECTRICAL CIRCUIT

The mechanical operation of the tester is controlled by the electrical circuit shown in Figure 9. The part of the circuit which controls the weight loading mechanism utilizes eight solenoids, S (Guardian No. 12 AC), for moving the eight weight arms into their vertical positions and 18 normally open switches for selecting the proper solenoids to apply the desired load. The keys operating the switches are locked by means of an additional solenoid, K, while the weight assembly is suspended. During the time the switches are free to be changed for selection of the desired load this part of the circuit is not excited.

Four of the solenoids are controlled by one decade of switches and the other four by a second decade. Four switches of each decade are single-pole, single- throw and control individual solenoids. Five other switches of each decade are either double-pole, single-throw or split-contact-throw (Micro-Switches BZ-3YLT were used) and control appropriate combinations of two solenoids. Thus with four weights the selection of any additive load in a decade is obtained by closing one of nine switches. One decade can adjust the load to correspond to specimen thicknesses from 0.1 to 0.9 millimeter in steps of tenth millimeter, and the other decade from 0.01 to 0.09 millimeters in hundredth millimeter steps. Thus the two decades can adjust the load for specimen thicknesses ranging from zero to 0.99 millimeter in hundredth millimeter steps. To close these switches it is convenient to use two decades of keys and the keyboard mechanism from a Friden calculator. This assembly is arranged so that the closing of one switch in a decade opens the others. The keyboard mechanism also provides a convenient device for locking the keys while the tester is in operation.
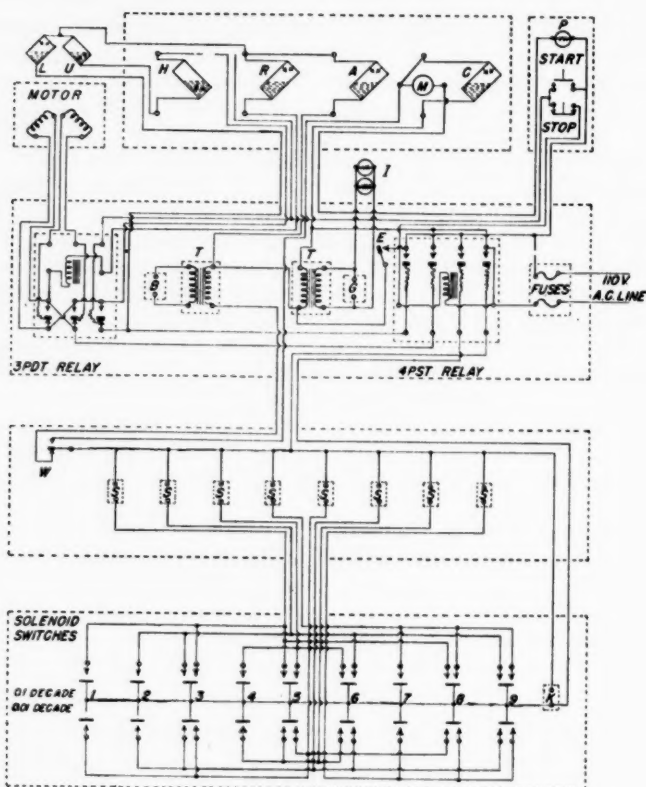
FIG. 9.—Electrical circuit for the rubber strain tester.

The positions of the switches and relays shown in the circuit are for the tester at rest.

A, switch for actuating single-stroke bell or gong, G, and lamps I.
B, bell or buzzer.
C, switch for stopping motor, M.
E, switch for manual operation of lamps, I, when the tester is not in operation.
G, single-stroke bell or gong.
H, switch for limiting the lift of the weight assembly after switch, W, is released.
I, lamps for illuminating upper bench mark during the observation period.
K, solenoid for locking the keyboard.
L, switch for opening 4PST relay when upper grip returns to starting position.
M; time cycle controller motor.
P, pilot-light for motor, M.
R, switch operating 3PDT relay to return upper specimen-grip to rest position at end of test.
S, solenoids for moving weight arms to their vertical position.
T, bell transformers.
U, switch for limiting upward travel of the upper grip.
W, SPDT switch for starting motor, M, and, when weight assembly is not freely suspended at time of measurement for ringing bell, B.

The electrical circuit which controls the weight loading mechanism is excited when the main relay (4PST, 110-volt AC, 6-ampere) is closed. This relay is closed by pressing the start button at the start-stop station. Once closed, the relay remains closed until the circuit to its exciting coil is broken either by the action of the limit switch, L, which opens when the upper grip returns to its starting position, or by the pressing of the stop button by the operator. Besides exciting the circuit controlling the wieght loading mechanism this relay starts the motor which lifts the upper grip and stretches the specimen.

When the weight assembly is freely suspended, a single-pole, double-throw precision snap switch, W, mounted on the weight loading mechanism starts the motor, M, on a time cycle controller. The function of the other position of this double-throw switch is to actuate a signal, which is described along with the signaling devices.

The sequence of operations after the weight assembly is freely suspended is controlled by a time cycle controller[5]. This controller consists of four mercury switches, which are opened and closed by the action of cams rotated by a synchronous, clock motor, M. The functions of the mercury switches are as follows:

1. The height switch, H, limits the height to which the weight assembly may be raised (approximately eight inches).

2. The signal switch, A, operates an alarm which indicates the time the measurement of elongation is to be made.

3. The reversing switch, R, actuates a three-pole double-throw relay which reverses the motor at the end of a test, permitting the specimen to retract and the weight assembly to come to rest.

4. The cycle switch, C, stops the time cycle controller at the end of the cycle. The four switches open and close at the following points in the revolution of the cams:

Switch	Opens	Closes
1 Height	9 degrees	355 degrees
2 Signal	284 degrees	248 degrees
3 Reversing	355 degrees	293 degrees
4 Cycle	360 degrees	5 degrees

A rotation of 360 degrees requires 80 seconds. To indicate when the controller is in operation, a pilot lamp, P (six volts, 0.15 ampere), is connected in series with the motor.

The signal switch of the controller closes the primary circuit of an eight-volt transformer, T. Connected to the secondary of the transformer is a single-stroke bell or gong, G, which serves to indicate when the elongation of the specimen is to be observed. The lamps, I, which illuminate the upper bench mark are connected to the same circuit. If the weight assembly is not freely suspended at the time the observation is to be made, the double-throw switch, W, attached to the weight loading mechanism connects a second transformer into the signal switch circuit. Connected to the secondary of this transformer is a vibrating bell or buzzer, B. This signal warns the operator that the observation is in error.

One of the limit switches, U, on the vertical track is used to protect the tester in case a specimen has an elongation greater than the limit of the tester or breaks before the motor of the time cycle controller starts. The other limit switch, L, breaks the circuit to the coil of the main relay at the end of each test when the upper grip returns to its starting position. This action breaks all the circuits except the one to the motor of the time cycle controller.

A switch, E, is provided for manual operation of the lamps, I, when illumination is desired for purposes other than the normal operation of the tester. For example, illumination is required when the zero position of the steel tape is being initially adjusted relative to the hair line on the upper positioners. This adjustment is conveniently accomplished by use of a separate millimeter scale held in the position of the specimen.

METHOD OF OPERATION

Three steps are involved in the strain test procedure: (1) preparation of the test-specimen from a rubber vulcanizate; (2) measurement of the cross-sectional area of the specimen to determine the load to be applied; and (3) measurement of the elongation of the specimen at a definite time after the load is applied.

PREPARATION OF SPECIMEN

From the usual test sheet of rubber vulcanizate, six inches square and about 0.075 inch thick, five specimens are cut by means of the die described previously. Using the marker described, bench marks ten centimeters apart are placed on each specimen. The marking compound should be of a contrasting color to that of the specimen; e.g., if the specimen is dark in color, red or white marks are convenient.

DETERMINATION OF LOAD

If the die is properly constructed and in good condition, the width of each specimen will be 0.254 inch (6.45 millimeters) to within 0.001 inch. Then only a measurement of the average thickness of each specimen by means of the gage also previously described is required to determine the cross-sectional area.

For measurements at a stress of 100 lbs. per sq. in., changes in thickness require changes in load, in pounds, which are numerically equal to the thickness in millimeters. Consequently, by setting the zero position of the dial gage to the numerical value of the fixed weight one needs merely to make the additive weights equal to the dial reading obtained with the different specimens. To obtain the same convenient arrangement at 200 lbs. per sq. in., the fixed load and each additive weight must be doubled. This doubling is accomplished by substitution of a different weight assembly. Analogously weight assemblies corresponding to any other desired stress can be used if desired. Alternatively the fixed weight can be manually adjusted for each stress, and a table used to obtain the key board settings corresponding to different dial gage readings.

MEASUREMENT OF STRAIN

The specimen is placed in the grips of the tester by the operator with the bench marks facing him. After depressing the proper keys controlling the additive weight, he presses the start button. This action engages the appropriate additive weights and stretches the specimen. The pilot light indicates when the weights become freely suspended and the time cycle begins. Fifty-five seconds later when the signal sounds, the operator holds the positioners against the specimen with his left hand and superimposes the hair line of the upper positioner on the upper bench mark by turning the hand wheel with his right hand. After this positioner is adjusted he superimposes the hair line of the lower positioner on the lower bench mark by sliding the positioner with his left hand. Approximately eight seconds is allowed for these two operations. The operator observes the elongation in percentage directly from the position of the hair line of the lower positioner on the millimeter tape. There is ample time to observe and record the elongation while the upper grip and weight assembly return automatically to their starting position. A new specimen can be inserted and the keys changed while the controller completes its cycle. Thus each specimen requires about $1\frac{1}{2}$ minutes of machine operation.

The operator, however, has about one minute of this time free, during which he could either operate a second machine or prepare specimens for measurement.

COMMENTS ON PERFORMANCE

The strain tester constructed in this laboratory has operated very satisfactorily for more than a year. In the usual stress-strain measurements the errors in testing have been found to be of the same order of magnitude as those arising in the preparation of the vulcanizate. On the other hand it has been found that the errors of testing with the strain tester are negligible in comparison to those arising in the preparation of the vulcanizate. This improvement in precision and accuracy of testing has been useful in both control and research testing. Data showing the improvement of precision were omitted from this paper, since they were part òf a separate publication[2] dealing with the use of the strain test for the evaluation of rubber vulcanizates.

An advantage of these tests in addition to the improved testing is the reduction in manhour requirements. This reduction is due in large part to obtaining the data in tabular form at the time of the test. At the same time the ease and convenience of the test has improved the morale of the testing personnel. The operation of the tester from a sitting position, the ease of changing weights, and the elimination of following two moving bench marks simultaneously have been the prime factors in this respect.

SUMMARY AND CONCLUSIONS

A tester for measuring the strain of rubber vulcanizates when subjected to a predetermined stress is described. The operation of the tester and a description of the apparatus for cutting and measuring the test specimens are presented. With this equipment routine determinations of a point on the stress-strain curve can be made with greater accuracy and precision than has hitherto been possible with the usual stress-strain equipment. This strain test also requires less labor than the customary stress tests.

REFERENCES

[1] The tester was designed and constructed at the request of the Subcommittee on Test Methods of the Committee on Specifications for Synthetic Rubbers, and was financed in part by funds transferred from the Office of Rubber Reserve, Reconstruction Finance Corporation.
[2] Roth and Stiehler, *India Rubber World* 118, 367 (1948); following paper in this issue of RUBBER CHEMISTRY AND TECHNOLOGY.
[3] These blades were supplied through the courtesy of the Gillette Safety Razor Co., 125 Granite St., Boston, Mass.
[4] Boston No. 35 Type.
[5] Model 602 of the Electric Switch Corporation.

PREPARATION OF DRIED LATEX FILMS *

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Various technical applications of latex call for the formation of a latex film and its drying by evaporation of the water in which the rubber is dispersed. The same problem is encountered also in the preparation of dried latex films, both uncompounded and compounded, for film testing for tensile, elongation, and other properties. Very frequently the preparation of such films is complicated by the development of surface cracks and ridges in the drying films[1], which mar the appearance of the films, detract from their strength, and make testing difficult and uncertain. These imperfections in the films generally arise from the formation of impervious surface skins on the drying latex. Such impervious skins lead to shrinkage and subsequent cracking of the films on the one hand, and to bubble formation on the other. The result is that the preparation of dried latex films by this method becomes a very slow process, which yields as a rule films of inferior appearance and quality.

It was found in this laboratory that many of the difficulties encountered in the preparation of latex films by evaporation can be overcome by appropriate control of humidity in the initial drying stages, and the use of an agent which prevents formation of the impervious surface skins on the drying latex. The agent found to be most suitable with alkaline latexes for the latter purpose is carbon dioxide gas. By utilizing moisture and carbon dioxide in a definite technique, films can be prepared from various latexes which are smooth and uniform in thickness and possess improved appearance and properties.

The purpose of this paper is to describe the technique developed for preparation of dried latex films by casting, and to give some results for tensile and elongation obtained on GR-S, Hycar, Neoprene, and natural latexes.

EQUIPMENT FOR FILM PREPARATION

Molds.—Most of the latex films prepared in this laboratory are cast in glass molds 30 cm. (10 inches) wide by 37.5 cm. (15 inches) long. The molds are made of double-strength window glass as a base, to which are cemented 1-inch strips of single-strength window glass to form a cavity 8 inches wide, 13 inches long, and 0.085 to 0.095 inch deep. Sodium silicate is used as a cement to seal the border strips to the base. Any excess silicate adhering to the glass is removed to leave a clean surface for the latex film.

For some work a larger mold is used, prepared in the same manner, but having a cavity 32 × 14 × 0.09 inches. This mold was made originally to find out whether a film of this size can be cast successfully, and to obtain a larger number of test strips from a single film. It was found that films of this large size can be prepared just as satisfactorily as smaller films. However, large glass molds are generally difficult to handle and level in a drying oven

and they tend to warp with time.   To obviate the last difficulty a metal mold was also tried.   It proved satisfactory in remaining true in shape and in accelerating film drying by better transfer of heat, but it was too heavy to handle conveniently, and gave some trouble in transmitting surface imperfections in the metal surface to the cast rubber film surfaces.

Drying ovens.—The oven employed for the setting of the latex films is a Thelco incubating oven made by the Precision Scientific Company.   This oven is equipped with double doors, the inner ones of glass through which the film can be observed, and is large enough to accommodate the 32 × 14 inch mold.   It is a gravity-convection type oven fitted with top and bottom vents, and is equipped with automatic temperature control.

The final drying or curing of the films was originally conducted in ordinary laboratory ovens of the gravity-convection type.   At present these operations are conducted in forced-draft circulation ovens.   The latter types of oven give a more uniform distribution of heat and better temperature control than the ordinary ovens, and hence more rapid and uniform drying or curing of films is possible in them.

Carbon dioxide supply.—The carbon dioxide gas used for conditioning the latex surface is ordinary cylinder gas.   It is fed to the setting oven by means of rubber tubing entering the oven through one of the top circulation vents.

Exhaust pump.—To expedite water removal in the latter stages of the film setting, a small exhaust pump is attached to the top of the oven.   By means of this pump the air circulation of the oven can be increased sufficiently to reduce the time of the film setting to about one half to one third of the time normally required without good air circulation.

STEPS IN FILM PREPARATION

The film casting and setting are carried out in the incubating oven kept at 50° C.   Before the latex is poured into the mold several preliminary operations must be carried out.   The first involves placing the mold, thoroughly cleaned and dried, in the oven and leveling it on the oven shelf.   It is imperative for good results that the mold be level; otherwise the drying is not uniform and the thickness of the film is variable.   Any open space on the oven shelf around the molds should further be covered with glass or metal plates so that the flow of heat is directed through the mold and convection of gases around the mold is prevented.   Failure to observe this precaution results frequently in considerable crazing of the film in the initial drying stages.

The next step is to saturate the oven with water vapor to prevent rapid drying of the latex during the initial setting period.   Such rapid evaporation promotes too rapid a skinning over of the latex, and leads to cracking and ridge formation.   The moisture saturation of the oven is accomplished simply by placing a pan of warm water on the bottom shelf of the oven below the mold.

When the oven is suitably saturated with moisture, and the mold is at oven temperature, the latex is poured into the mold.   The latex introduced may be straight latex without any additions, or latex that has been compounded. Care should be exercised in pouring the latex so as to avoid introduction of bubbles.   The amount introduced depends on the thickness of film desired, and can be estimated by trial.   In any case, the volume poured into the mold must be sufficient to cover the entire bottom of the mold to a depth sufficient to give the requisite thickness of dry film.   It depends on the size of the mold and the solids content of the latex.

Immediately after the introduction of the latex the oven is closed, the bottom vents are plugged, and carbon dioxide admission is started through the top vent. To prevent the carbon dioxide stream from hitting and disturbing the latex surface, it is best to place a glass baffle plate between the carbon dioxide entrance and the latex mold. By this means the gas is dispersed throughout the oven without impinging directly on the latex. Unless this precaution is observed, the latex surface is disturbed and the resulting film develops a ripple appearance.

The initial rate of carbon dioxide entrance must be sufficient to ensure rapid saturation of the oven chamber with this gas so that formation of the impervious film surface, which is detrimental to good film formation, can be prevented. Within a short time of the carbon dioxide entrance the latex surface acquires a lighter hue, and the rate of carbon dioxide flow can then be diminished. Under the further action of the carbon dioxide, and in the presence of the water vapor, the surface gradually assumes a dull cast which is indicative of the formation of the desired type of surface skin. Completion of this phase in the skin formation is evidenced by a uniform spread of this dull cast over the entire latex surface. At this stage the carbon dioxide addition is stopped, the pan of water is removed from the oven, the bottom vents are opened, and the film is left undisturbed for an hour or more before the drying rate is accelerated by initiating gentle air circulation through the oven by means of the suction pump. At the end of some time the rate of air circulation can be increased substantially, and continued until the film is set. Setting is said to be completed when the film of rubber is sufficiently rigid to be removed from the mold and handled for final drying.

As an uncompounded latex film dries in setting, it undergoes a regular series of transformations. First it loses its opalescence and takes on a dull appearance. After a while the film starts to develop a transparency analogous to viscous gel. Finally, as evaporation proceeds and the film begins to set, the transparency disappears slowly, and the film starts to become opaque. Setting is complete when the opacity permeates the entire film. The film is ready then to be removed from the mold. With compounded latexes these changes are more difficult to observe because they are masked by the opacity of the compounding ingredients.

Experience has shown that it is best to remove the films from the molds right after setting rather than to let them dry completely in the molds. When left in the molds until dry the films tend to develop strains, and show a tendency to stick tenaciously to the glass surface. Strongly adhering films can be loosened by introducing a little water under the film edge, but then the films have to be redried, and the strain damage is done. It is best, therefore, to complete the final drying of uncompounded films, or drying and curing of compounded films, in a separate oven, preferably one with forced draft circulation. On final drying the uncompounded rubber films become transparent, whereas the compounded films are opaque. Uncompounded films are dried at 100° C, whereas compounded films are dried and cured at whatever temperature is necessary.

The above technique of film preparation has been applied successfully to GR-S, Hycar, Neoprene, and natural latexes. Apparently the size of the film is no limitation, for small as well as large films of excellent quality have been prepared. Although in all cases the general procedure followed was as described above, the actual periods of time to which films of different latexes were subjected to various phases of the process varied. Table I summarizes

TABLE I

DETAILS OF FILM PREPARATION PROCEDURE FOR UNCOMPOUNDED LATEXES

Latex	Type III	Hycar OR-30	Hycar OR-40	Neoprene 571	Natural Latex
Solids (%)	36–40	30	40	50	60
Time of CO_2 treatment (hours)	ca. 1	1–1.5	1–1.5	30 sec.	5 min. to ca. 1 hour
Time of moisture treatment (hours)	ca. 1	1–1.5	1–1.5	ca. 0.5	ca. 1
Time of drying without circulation (hour)	ca. 1	ca. 1	ca. 1	ca. 1	ca. 1
Time of drying with circulation (hours)	10–12	10–12	10–12	10–12	ca. 2
Total setting time (hours)	12–14	12–14	12–14	10–12	ca. 4
Final drying time at 100° C (hours)	ca. 24	ca. 24	ca. 24	ca. 24	Generally none
Total time for film preparation (hours)	ca. 36	ca. 36	ca. 36	ca. 36	ca. 4

the conditions found to be optimum for preparation of uncompounded latex films. Generally 1 to 1.5 hours of carbon dioxide treatment are required for all latexes tried except Neoprene-571 and natural latexes. Neoprene-571 coagulates completely when subjected to carbon dioxide for 1 minute, and hence only about a 30-second flash admission of the gas can be used. However, even this short exposure to the gas is sufficient to yield an improved film of Neoprene. With natural latexes the approximately 1-hour exposure to carbon dioxide has been found necessary when the ammonia content of the latexes was low. On the other hand, when the ammonia content was appreciable, satisfactory skinning over conditions could be obtained in as short an exposure to carbon dioxide as 5 minutes. Excessive carbon dioxide treatment in the latter instances resulted in the formation of a coagulated gel which resembled very closely the type of gel obtained on treatment of such latexes with appreciable quantities of ammonium salts.

The optimum time of moisture treatment was found to range from 0.5 to 1.5 hours, depending on the latex. In turn, the drying time of about 1 hour without air circulation has been found necessary because in its early stages the surface film is too weak to withstand rapid evaporation. Once this surface film toughens somewhat, the rate of water removal can be accelerated.

In all cases except natural latex approximately 12 to 14 hours are required to set a film. With natural latex the setting time is very rapid, and at the end of about 4 hours the latex film is not only set but dry as well. Generally films once set are dried at 100° C for about 24 hours. The maximum tensile strengths are usually observed at the end of this drying period in all cases except natural latex, which showed better tensile strengths at the end of the 4-hour setting time than on subsequent drying.

With compounded films the carbon dioxide–moisture treatment periods are essentially the same as those given in Table I for uncompounded films, but the setting times are longer, usually about 24 hours, for Type III latex. Furthermore, compounded films do not seem to require subsequent drying in addition to the heating required to obtain optimum cure, i.e., generally about 1 to 1.5 hours at 100° C.

RESULTS AND DISCUSSION

The use of carbon dioxide and moisture regulation in film preparation was found in every case to yield films superior to those prepared by other tech-

niques. Controls run on the various latexes under conditions which were similar, but without carbon dioxide and moisture present, yielded in general films of poor appearance and with surface cracks. On the other hand, the films prepared as described were smooth and without the imperfections ordinarily observed, and showed in every case higher tensile strengths than the corresponding controls. Table II shows data on uncompounded films to substantiate this statement. It is evident that the carbon dioxide–moisture treatment leads to a film not only improved in appearance but also of better physical characteristics. The two factors may well be connected, for a film without strains, cracks, ridges, or bubbles should be able to resist tension better than one with flaws.

The action of carbon dioxide in yielding satisfactory skin formation on latex film surfaces suggests that other acidic gases as well may be suitable for this purpose. This is actually the case. Hydrogen chloride gas was found to work well on Type II latex. However, from a corrosion standpoint carbon dioxide is to be preferred to other acidic gases. Alkaline gases should also be

TABLE II
TENSILE DATA ON UNCOMPOUNDED FILMS

	New method		Control	
Latex	Tensile strength (lb./sq. inch)	Elongation (%)	Tensile strength (lb./sq. inch)	Elongation (%)
Type III	800–1200	1400–1700	700	1600+
Hycar OR-40	760	2000+	390	2000+
Neoprene-571	2800	1200	1520	1000
Natural	1800	1200	1500	1200

applicable to acidic latexes prepared with cationic emulsifiers.

Preparation of rubber films from latex by the method described here generally does not require any preliminary treatment of the latex, such as thickening. However, indications are that the latex must be sufficiently alkaline to absorb some carbon dioxide for satisfactory surface skin formation. When the alkalinity is too low good film formation is difficult. This is exemplified by attempts to produce films from Type II latexes. Such latexes have as a rule relatively low pH's and their tendency to good skin formation in presence of carbon dioxide is poor. When, however, the pH is raised to about 10.5 by addition of sodium hydroxide, the formation of satisfactory films in presence of carbon dioxide is considerably improved.

Many compounded latex films have also been prepared by the carbon dioxide–moisture technique. Their behavior was found to be essentially similar to that of the uncompounded films. As an example may be cited the preparation of a rubber film from Type III latex compounded with Vanderbilt Dispersion C-199. This compounded latex skinned over in 1 hour in presence of carbon dioxide and water vapor, and set and dried in 24 hours. On curing at 100° C for 1.5 hours the film gave a tensile of 2200 pounds per square inch and an elongation of 800 per cent.

REFERENCE

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PROPERTIES OF EBONITE*. XXVIII. INFLUENCE OF LIGHT-ABSORBENT PIGMENTS ON ELECTRICAL SURFACE DETERIORATION DURING EXPOSURE TO LIGHT

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To determine whether the use of light-absorbent pigments in ebonite would reduce the surface deterioration on exposure to light, the following samples were tested for surface resistivity before and after exposure to light for various periods:

Mixing:	H58A	H58B	H61A	H61B	H61C
Smoked sheet rubber	68	—	68	68	68
Pale crepe	—	68	—	—	—
Sulfur	32	32	32	32	32
MPC black	—	—	10	—	—
Ferric oxide	—	—	—	30	—
Lead titanate	—	—	—	—	50

The H58 samples were vulcanized for 3 hours and the H61 samples for 5 hours at 155° C.

Lead titanate has been stated[1] to be very efficient in absorbing ultraviolet radiations. The pale crepe mixing was included to compare the magnitude of any changes in surface deterioration introduced by the incorporation of pigments with the small variations among different raw rubber mixings.

For testing the effect of light, the specimens were enclosed in a box with a quartz window, through which air at 75 per cent relative humidity was circulated continuously. The artificial light source was an incandescent-cathode quartz mercury-vapor lamp; the light emission was 950 candles. The specimens were exposed 28 cm. away from the lamp. Two test-pieces were prepared from each mixing and two exposure boxes were filled, each containing one test-piece from each mixing. One box was exposed to north daylight, the other to the mercury-vapor lamp. Measurements of surface resistivity were made, by the method of Church and Daynes[2], after various periods of exposure, in each case on the day following exposure so as to allow attainment of equilibrium with the 75 per cent humidity. Graphs were plotted showing the logarithm of resistivity against period of exposure in hours (see Figure 1), and the following figures were obtained from these graphs for convenient comparison of the samples.

	Exposure to mercury-vapor lamp			Exposure to north daylight		
Sample	Initial surface resistivity (ohms)	Period required for resistivity to fall to 10^{14} ohms (hrs.)	Resistivity after 36 hours' exposure (ohms)	Initial surface resistivity (ohms)	Period required for resistivity to fall to 10^{14} ohms (hrs.)	Resistivity after 36 hours' exposure (ohms)
H58A, 3 hrs.	3×10^{18}	$7\frac{1}{2}$	3×10^{8}	1×10^{19}	17	3×10^{8}
H58B, 3 hrs.	4×10^{18}	7	2×10^{8}	$>10^{19}$	19	5×10^{8}
H61A, 5 hrs.	2×10^{18}	$7\frac{1}{2}$	6×10^{9}	1×10^{18}	20	8×10^{11}
H61B, 5 hrs.	1×10^{18}	6	1×10^{10}	1×10^{17}	16	1×10^{11}
H61C, 5 hrs.	2×10^{18}	7	2×10^{9}	1×10^{17}	11	2×10^{10}

Measurements of resistivity above 10^{17} ohms are not very reliable, since they are near the upper limit of the measuring apparatus. Hence the large differences between the initial resistivity figures for duplicate test-pieces are not surprising.

SURFACE DETERIORATION OF BLANK AND PIGMENTED EBONITE
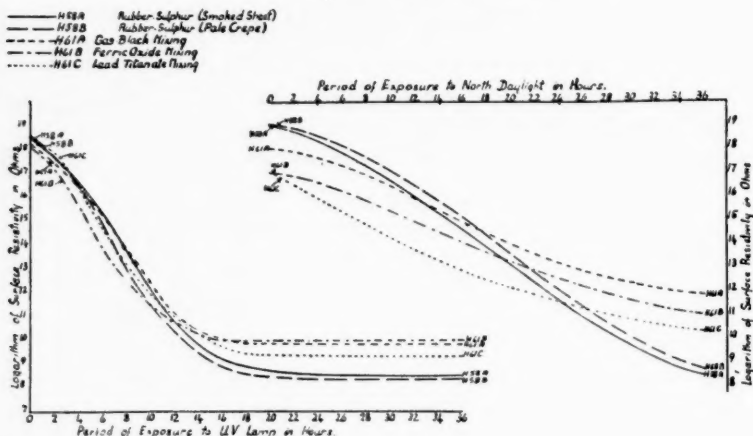
Fig. 1.

The pigments do not cause any remarkable improvements in the resistivity after exposure. The periods of exposure to the mercury-vapor lamp required to reach 10^{14} ohms are approximately the same for all the five types of ebonite. The periods required in north daylight show larger differences, but even the longest (gas black sample) does not represent a practically useful improvement.

The later part of the resistivity curves indicates slight superiority in the pigmented ebonites. This can be best seen from the curves for exposure to the lamp, which are more nearly complete after 36 hours' exposure than are the daylight curves. Judging by the resistance after 36 hours' exposure to the mercury-vapor lamp, the iron oxide sample (H61B) appears to be the best, followed by the gas black sample (H61A), the lead titanate sample (H61C), with the two blank mixings (H58A and B) worst.

A further point which these experiments were designed to elucidate was whether the relative effects of the mercury-vapor lamp on surface deterioration of different ebonites were comparable with those of daylight. The intensity of the daylight in these experiments was not measured; hence no numerical relationship between the activities of the two sources can be found, but it is clear that the main effect of using the lamp instead of daylight is to accelerate the deterioration; it does not introduce any striking differences among the samples.

SUMMARY

The incorporation of gas black, ferric oxide, and lead titanate, which absorb actinic rays, into rubber-sulfur ebonites did not reduce the rate of electrical

surface deterioration appreciably. It increased the final equilibrium resistivity, but not sufficiently for the increase to be of much practical value.

This result confirms the conclusion from a study of the mechanism of surface deterioration[3] that a light-absorbent pigment is unlikely to be effective in retarding deterioration because its particles are relatively large and far apart in comparison with the thickness of the surface layer responsible for the deterioration.

The use of the mercury-vapor lamp causes a more rapid deterioration than daylight, but does not appear to alter the order in which the samples range themselves.

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PROPERTIES OF EBONITE. XXIX. THE ABSORPTION SPECTRUM OF EBONITE

E. H. DOCK, B. D. PORRITT, AND W. H. WILLOTT

The absorption spectrum of ebonite has some practical interest, because the absorption of light causes the surface to deteriorate. A knowledge of the absorption spectrum should help in discovering which are the harmful rays. Published information[1] hitherto appears to be limited to radiation of long wave length, *i.e.*, thermal or infrared.

The present note describes experiments on rubber-sulfur (65:35 or 68:32) compositions vulcanized for about 5 hours at 155° C. Owing to the great opacity of ebonite, it is necessary to work with very thin specimens. Various methods of obtaining these suggest themselves: (1) grinding down a small thin sheet; (2) cutting thin shavings; (3) vulcanizing as of a thin film between glass or quartz plates; (4) vulcanizing a film of rubber, deposited on glass or quartz, by immersion in molten sulfur; (5) vulcanizing a deposited film of a rubber-sulfur mix by heating in an inert gas. Methods (1), (2) and (5) have so far been found the most satisfactory. In method (2) it is advantageous to soften the material by swelling, *e.g.*, in nitrobenzene; the swelling liquid can then be removed by extraction with a volatile solvent. Methods (1) and (2) have the advantage of enabling specimens to be obtained from larger pieces that can be analyzed or submitted to other tests.

The first observations on the absorption spectrum, made with a small direct-vision grating spectroscope, showed that the ebonites transmitted light chiefly in the red, yellow, and green regions, strong absorption commencing in the blue and extending to the violet end of the visible spectrum. The wave length at which strong absorption became noticeable, however, was not sharply defined, and varied with the thickness of the specimen. The following approximate values for this wave length were found.

Specimens about 0.05 mm. thick (prepared by cutting after swelling in nitrobenzene)   5,200 to 5,300 Å (in bluish-green region)

Specimen 0.01 mm. thick (shaving produced on shaping machine)   4,500 Å (blue-violet)

To obtain more precise results, a specimen 0.055 mm. thick was prepared by grinding down a small thin sheet with a very fine abrasive; this was examined by S. Judd Lewis, using a spectrophotometer, with the following results.

Wave length (Å)	Percentage light transmitted
7,000 (red)	about 25–30
6,130 (red)	10
5,815 (yellow-green)	5
5,710 (green)	2.9
5,660 (green)	2
5,590 (green)	0.9
5,450 (green)	0.4
5,180 (blue-green)	<0.01

Practically no light was transmitted below a wave length of 5,180 Å; an intense line at 4,950 Å was very feebly transmitted. There was no sign of selective absorption suggestive of an absorption band. It is probable that the film would transmit some infrared radiation.

As the surfaces of the specimen, although smooth, were not polished, some of the apparent absorption must have been due to scattering. These quantitative results show that even in those parts of the spectrum, where, to the eye, the material seems relatively transparent, the transmission is only small. The results agree with the previous observations in showing that with specimens about 0.05 mm. thick the very strong absorption commences around 5,200 Å. The observations on the specimen 0.01 mm. thick, show that absorption becomes even stronger at shorter wave lengths.

<div align="center">REFERENCES</div>

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PROPERTIES OF EBONITE. XXX. INFLUENCE ON PROPERTIES OF EBONITE OF THE TYPE OF RAW RUBBER USED, WITH SPECIAL REFERENCE TO PURIFIED RUBBERS

D. G. FISHER, J. R. SCOTT, AND W. H. WILLOTT

INTRODUCTION

This report describes a continuation of the Joint Ebonite Research undertaken by the Electrical Research Association and the Research Association of British Rubber Manufacturers, with the collaboration of the London Advisory Committee for Rubber Research (Ceylon and Malaya). The experiments were made to determine to what extent the properties of ebonite as a dielectric can be improved by using raw rubbers specially prepared or treated to have a reduced content of electrolytes and(or) water-absorbent substances.

Various methods of producing such raw rubbers have been developed, the rubbers being used especially in making cable dielectrics on account of their improved electrical properties and reduced water absorption[1].   The object of the present experiments was to determine to what extent the removal of electrolytes and(or) water-absorbent substances would be of advantage in making unloaded ebonites for electrical purposes.   To show the effect of excessive quantities of these substances, tests were made also with a whole-latex rubber, this containing all the water-soluble components of the original latex.

Attention has been directed chiefly to the electrical properties and water absorption of the ebonites, since small changes in the nonrubber components of the rubber are not likely to alter the mechanical properties.

RAW RUBBERS EXAMINED

The rubbers used in this investigation were as follows, samples F and G being supplied by the London Advisory Committee for Rubber Research (Ceylon and Malaya).

A. Smoked sheet.
B. First latex pale crepe.
C. Fine hard para (washed and dried).
D. Deproteinized rubber prepared by treatment of the latex to hydrolyze the proteins, and removal of the products of hydrolysis.
E. Powdered (whole-latex) rubber; latex is evaporated to dryness in the form of isolated droplets, and the resulting rubber granules dusted with zinc stearate to prevent adhesion[2].
F. Low water-absorption rubber, L258/2, prepared by treating ammoniated 34.8 per cent latex with papain solution, activated by potassium cyanide, coagulating with magnesium chloride and sodium fluosilicate, soaking the coagulum in water, and then crepeing.
G. Low water-absorption rubber, mixture of samples L156/6 and L156/7, prepared by coagulating diluted latex ($\frac{3}{4}$ pound of rubber per gallon) with 1 per cent formic acid and soaking the coagulum for 72 hours and 96 hours, respectively, in water.
H. Smoked sheet, washed and dried.
J. Deproteinized rubber prepared by heating latex with alkali to solubilize the nitrogen, concentrating by creaming or centrifuging, diluting the concentrate, coagulating, and finally washing and drying the coagulum[3].
K. Deproteinized rubber similar to J, but with addition of antioxidant.

The smoked sheet, crepe, and para represent standard market grades, and deproteinized rubbers D and J were being produced commercially before 1942; F and G were experimental samples; J and K were small samples from which it was only possible to prepare one sheet of ebonite, used for the power factor specimen.

Water absorption tests were made on the raw rubbers for correlation with the corresponding data for the ebonites made from them.   The measurements were made by exposing the thinly sheeted rubber to an atmosphere of 97 per cent relative humidity at 20° C, using the British Standard technique[4].   As the absorption usually continued to increase slowly after the initial rapid rise, apparently owing to oxidation, it was convenient to extrapolate the upper part of the time/absorption curve back to the absorption axis so as to obtain

the initial absorption, which forms a convenient figure for comparison purposes (results are included in Table 7).

PREPARATION OF THE EBONITES

The ebonites were made from 68:32 rubber/sulfur stocks, vulcanized in moulds to give sheets about 0.25 in. thick. Vulcanization was in an autoclave press at 155° C, for periods of 3, 5, and 8 hours. Fuller details of the method have been given by Church and Daynes[5]. In the present experiments the ebonites had to be vulcanized in four separate batches, namely, A, B, C, and E; D and H; F and G; J and K.

RESULTS OF TESTS ON THE EBONITES

CHEMICAL ANALYSIS

Ash was determined by incinerating the ebonite at about 500° C. Total sulfur was estimated by the Carius method, and the acetone extract by extracting the powdered ebonite for 16 hours in a drip-type thimble, the extract being dried for 1 hour at 65° C. The sulfur in the acetone extract (free sulfur) was estimated by oxidation with bromine[6]. The vulcanization coefficient (parts of sulfur combined with 100 parts of rubber hydrocarbon) was calculated from the combined sulfur taken as the difference between total sulfur and sulfur in extract. Organic acetone extract is the acetone extract minus the sulfur contained in it. All results except vulcanization coefficient are expressed as percentages on the ebonite (see Table 1).

The high ash figure for the ebonite from whole-latex rubber (E) was to be expected, since this type of rubber contains relatively large amounts of mineral substances (ash 1.1 per cent). The ash figures for the ebonites made from smoked sheet, crepe, and para (A, B, C, and H) are higher than would be expected, probably due to traces of the French chalk used for dusting the unvulcanized stocks. The special samples (D, F, G, J, and K) give similar values.

Examination of the vulcanization coefficients, together with the total sulfur contents of the various mixings, shows that all the rubbers except the deproteinized sample D have much the same rate of vulcanization, the range of variation being only some 20 per cent. Rubber D, however, shows a vulcanization rate 40 per cent greater than the average of the others. The order of increasing vulcanization rate appears to be A, B, E, C, F and G, H, D. As this grouping corresponds to the batches in which the ebonites were vulcanized, some of the observed variation in rate of vulcanization may be due to slight differences in vulcanizing temperature (2° C variation would account for the observed difference between A and H).

The organic acetone extracts of the ebonites made from the low water-absorption rubbers F and G are low; that of the whole-latex rubber ebonite (E) is high.

PLASTIC YIELD

Plastic yield tests, used mainly as an additional indication of rate of vulcanization, were made by the R.A.B.R.M. torsion method[7], the results being included in Table 1.

Judging by the rate of approach to the maximum yield temperature, representing the substantially fully vulcanized material, the order of increasing rate of vulcanization is: A, B, C, E and H, D; F and G cannot be placed owing to the absence of the 3-hour vulcanizates. There is thus agreement with the

TABLE 1

ANALYSES AND PLASTIC YIELD RESULTS FOR EBONITES MADE FROM
VARIOUS RUBBERS

Rubber	Vulcan-ization (hrs.)	Ash (%)	Total sulfur (a) (%)	Acetone extract (%)	Sulfur in extract (%)	Organic acetone extract (%)	Vulcan-ization coeffi-cient	Yield tempera-ture (° C)	Slope (c), angular degrees per 10° C
A	3	—		7.4	5.5	1.9	40.1	45	5.8
	5	0.45	31.9	3.65	2.05	1.6	45.4	76	8.0
	8	—		3.3	1.7	1.6	45.9	81	8.3
B	3	—		5.55	4.0	1.55	40.9	58	7.1
	5	0.33	31.3	3.5	2.1	1.4	43.7	80	10.7
	8	—		3.2	1.7	1.5	45.3	84	13.2
C	3	—		4.85	3.6	1.25	41.9	63	12.4
	5	0.33	31.6	3.05	1.8	1.25	44.6	81	9.5
	8	—		2.6	1.4	1.2	45.2	84	11.9
D	3	—		2.9	1.65	1.25	44.4	77	11.6
	5	0.35	31.4	2.5	1.25	1.25	45.0	81	9.4
	8	—		2.4	1.15	1.25	45.2	83.5	11.0
E	3	—		6.3	3.7	2.6	44.9(b)	74	8.9
	5	0.78	32.5	5.15	2.7	2.45	46.4	80.5	12.0
	8	—		4.95	2.5	2.45	46.7	81	10.7
F	5	0.52	31.6	2.7	1.85	0.85	44.2	79.5	9.4
	8	—		2.2	1.4	0.8	44.9	83	11.6
G	5	0.36	31.3	2.6	1.75	0.85	43.9	79	10.2
	8	—		2.5	1.4	1.1	44.4	84	11.1
H	3	—		4.1	2.6	1.5	45.3	73	8.8
	5	0.25	32.4	3.45	1.95	1.5	46.3	80	9.5
	8	—		3.4	1.8	1.6	46.5	83.5	10.5
J	5	0.46	—	—	—	—	—	—	—
K	5	0.49	—	—	—	—	—	—	—

(a) Average of determinations on the three vulcanizates.

(b) Owing to the large amount of nonrubber components in rubber E, and the uncertain extent to which these react with sulfur, the calculated vulcanization coefficients for the ebonites are only approximate.

(c) Slope of the straight steeply-rising part of the temperature/yield curve above the yield temperature.

analyses in that D is quickest, H next, and A and B slowest. The differences in rate of vulcanization shown by the plastic yield results are of about the same magnitude as deduced from the analyses.

The yield temperature of the fully vulcanized ebonites ranges only from 81° to 84° C, all except A and E being between 83° and 84° C. The results for slope are again much alike, except for the rather lower values given by the smoked sheet ebonites (A). Thus, no substantial improvement in resistance to deformation at high temperatures is obtained by using the special types of raw rubber.

PERMITTIVITY AND POWER FACTOR

Permittivity and power factor were measured on a modification of the Schering bridge, using mercury electrodes incorporating a guard-ring device, at a

frequency of 10^6 cycles per second; the measurements were made in the following order: (1) at 20° C as received; (2) at 60° C (see below); (3) at 20° C next morning (see below); (4) at 20° C after conditioning at 90 per cent relative humidity for 3-4 months; (5) at 20° C after further conditioning for 3-4 months at 75 per cent relative humidity. Tests (2) and (3) were made only on the 8-hour vulcanizates of A, B, C, E, F, and G and the 5-hour vulcanizate of E.

The ebonite sheets, originally about 6 mm. thick, were turned down so that the average thickness of those from rubbers A, B, C, E, F, and G (excluding A, 8 hours) was 0.235 cm., the extremes being 0.217 and 0.270 cm.; those from rubbers D and H averaged 0.146 cm. Sample A, 8 hours, was reduced unintentionally to 0.112 cm.; as the behavior of this specimen, with varying humidity, did not differ materially from that of the other samples made from the same rubber, it may be presumed that most of the specimens attained equilibrium with the humidities described under tests (4) and (5) within the period of 3–4 months.

It may first be noted from Table 2, that whole-latex rubber (E) gives ebonite with a rather higher permittivity and much higher power factor than the other rubbers, thus showing the adverse effect of excessive percentages of the electrolytes and water-absorbent substances in the latex serum. The ebonites made from this rubber behaved in a somewhat irregular manner, which was confirmed by experiments on the 5-hour vulcanizate at 60° C and lower temperatures. This sample gave a lower power factor at 60° C than between 45° and 55° C, but returned to its original condition at room temperature.

Both permittivity and power factor are often higher in the final test after conditioning at 75 per cent relative humidity than when tested at 75 per cent relative humidity in their original condition, and with J and K they are actually higher than in the preceding test at 90 per cent relative humidity. Possible causes are: (1) the effect of exposure to 90 per cent relative humidity may not be eliminated by the subsequent conditioning at 75 per cent relative humidity; (2) when new, the samples would probably contain less moisture than corresponds to equilibrium with 75 per cent relative humidity; (3) the electrical properties might show a progressive change with time, independently of variations in ambient humidity. The results for the E, J, and K ebonites suggest the existence of such secular variation, because the power factor continues to increase during the final conditioning at 75 per cent relative humidity, instead of showing the expected decrease due to a change to lower humidity. In the E series this secular variation seems to depend on the vulcanizing time and(or) the thickness of the specimen (the 3-, 5-, and 8-hour samples were 0.270, 0.237, and 0.222 cm. thick, respectively).

It is clearly not possible, from the present results, to decide to what extent these three factors are responsible for the observed effects; the apparent existence of secular variation calls for further study. Since, however, the tests after prolonged conditioning at 75 per cent relative humidity should be more strictly comparable among themselves than the tests on the new samples, the former will be used in comparing the rubbers. The heating to 60° C, applied to some samples before the 75 per cent relative humidity conditioning, produces no appreciable permanent effect, and therefore does not invalidate the comparison

Most of the rubbers give ebonites with very similar permittivities, all the values for smoked sheet (A), crepe (B), para (C), deproteinized rubber (D), and washed smoked sheet (H) lying between 2.82 and 2.87. The low water-

absorption samples F and G and the deproteinized samples J and K give lower values (about 2.76–2.80). The whole-latex rubber (E) gives high values.

The power factor varies with period of vulcanization, so that it is necessary to take values corresponding to a definite state of vulcanization, as indicated by the analyses and plastic yield tests. The following figures relate to a state equal to that produced by 5 hr. vulcanization in the case of an average rubber:

A	B	C	D	E	F	G	H	J	K
1.11	1.09	1.17	0.96 ·	2.34	0.92	0.87	1.03	0.97	1.06

The deproteinized (J and D) and low water-absorption (F and G) rubbers give the best results; the deproteinized rubber K is little better than the normal rubbers A, B, and C, though J and K give exceptionally good figures in the initial tests (see Table 2). Para (C) seems slightly inferior to smoked sheet and crepe (A and B), and washing smoked sheet produces a small improvement (compare H and A).

The above comparison relates to samples brought more or less to equilibrium with normal conditions (20° C and 75 per cent relative humidity). The effects of exposure to high humidity and high temperature must now be considered. Judging by the changes in permittivity on exposure to 90 per cent relative humidity and then again to 75 per cent relative humidity, the specially prepared or treated rubbers D, F, G, and H give, on the whole, more stable ebonites than the ordinary types (A, B, and C). Apart from the whole-latex sample (E) the changes do not exceed 0.05. J and K cannot strictly be brought into this comparison, as the secular effect seems to have masked the true humidity effect; however, in passing from 75 per cent relative humidity to 90 per cent relative humidity the permittivity is unchanged, suggesting a good stability to humidity variations (see, however, the remarks below regarding the change in power factor with humidity).

Power factor likewise is higher at the high humidity. Averaging the results for the different vulcanizing periods gives the following values for the decrease in power factor on passing from 90 to 75 per cent relative humidity (E, J, and K are omitted because they show an increase):

A	B	C	D	F	G	H
0.10	0.03	0.07	0.04	0.05	0.05	0.12

The ebonites made from crepe (B), deproteinized rubber D, and the low water-absorption rubbers F and G, appear more stable than the others.

With J and K it is only possible to judge from the less reliable change produced by increasing the humidity from 75 to 90 per cent. By this criterion, these ebonites appear rather unstable, since they show power factor increases of 0.13 and 0.09, respectively, whereas none of the other ebonites except A and C increase by more than 0.05, taking an average for the different vulcanizing periods. This doubtless arises from the superposition of the secular change on the humidity effect.

Raising the temperature from 20° to 60° C increases the permittivity of the ebonites made from the ordinary rubbers (A, B, and C) by 0.05–0.07, and that of the low water-absorption samples (F and G) by 0.03–0.04. Power factor is increased by 0.27–0.36 with A, B, and C, but by only 0.16–0.17 with F and G. The specially prepared rubbers therefore give more temperature-stable ebonites than the ordinary rubbers. The whole-latex sample E is anomalous in that

TABLE 2
PERMITTIVITY AND POWER FACTOR OF EBONITES MADE FROM VARIOUS RUBBERS

Rubber	Temp. (° C)	Relative humidity (%)	Permittivity Vulcanization 3 hrs.	5 hrs.	8 hrs.	Power Factor (%) Vulcanization 3 hrs.	5 hrs.	8 hrs.
A	20	75	2.81	2.82	2.81	0.85	1.03	1.14
	60	75	—	—	2.86	—	—	1.46
	20	75	—	—	2.81	—	—	1.14
	20	90	2.86	2.87	2.84	1.06	1.17	1.26
	20	75	2.83	2.84	2.85	0.98	1.08	1.14
B	20	75	2.82	2.82	2.86	1.00	1.10	1.10
	60	75	—	—	2.93	—	—	1.36
	20	75	—	—	2.86	—	—	1.10
	20	90	2.86	2.87	2.87	1.07	1.14	1.13
	20	75	2.84	2.85	2.85	1.03	1.09	1.12
C	20	75	2.80	2.81	2.85	1.01	1.16	1.15
	60	75	—	—	2.92	—	—	1.42
	20	75	—	—	2.85	—	—	1.16
	20	90	2.84	2.86	2.85	1.16	1.24	1.25
	20	75	2.82	2.82	2.83	1.08	1.17	1.19
D	20	75	2.81	—	2.85	1.03	—	1.01
	20	90	2.82	—	2.86	0.98	—	1.01
	20	75	2.83	—	2.87	0.96	—	0.96
E	20	75	2.91	2.95	3.04	1.44	1.57	2.17
	60	75	—	3.14	3.18	—	2.27	1.81
	20	75	—	2.95	3.03	—	1.58	2.18
	20	90	3.03	3.06	3.11	2.23	2.29	2.20
	20	75	3.03	3.05	3.08	2.30	2.39	2.34
F	20	75	—	2.78	2.83	—	0.95	0.91
	60	75	—	—	2.86	—	—	1.08
	20	75	—	—	2.83	—	—	0.92
	20	90	—	2.81	2.81	—	1.00	0.96
	20	75	—	2.79	2.80	—	0.92	0.94
G	20	75	—	2.75	2.81	—	0.89	0.89
	60	75	—	—	2.85	—	—	1.06
	20	75	—	—	2.81	—	—	0.90
	20	90	—	2.79	2.79	—	0.92	0.92
	20	75	—	2.77	2.78	—	0.87	0.87
H	20	75	2.84	—	2.84	1.11	—	1.11
	20	90	2.86	—	2.85	1.15	—	1.15
	20	75	2.87	—	2.86	1.02	—	1.04
J	20	75	—	2.75	—	—	0.80	—
	20	90	—	2.75	—	—	0.93	—
	20	75*	—	2.77	—	—	0.97	—
K	20	75	—	2.73	—	—	0.84	—
	20	90	—	2.73	—	—	0.93	—
	20	75*	—	2.76	—	—	1.06	—

* Before the 75 per cent relative humidity conditioning treatment the relative humidity accidentally rose to 100 per cent for a period.

at high temperature the power factor of the 5-hour vulcanizate increases; that of the 8-hour vulcanizate decreases.

Summarizing these results, the use of specially prepared raw rubber gives a definite improvement in the dielectric properties of ebonite.   Thus, the loss factor (permittivity × power factor) of ebonite made from the special rubber G is 2.41 as compared with 3.10–3.30 for ebonites made from the ordinary rubbers—smoked sheet, crepe, and para (see Table 8); sample J in its initial condition has a loss factor of only 2.20, but seems to deteriorate with the passage of time.   Moreover, the detrimental influence of high humidity and high temperature on the electrical properties is generally reduced.

BREAKDOWN STRENGTH

Although it was not possible to test more than two specimens from each mixing, the results suffice to show whether or not the special rubbers give marked advantage.   Samples having the same vulcanization periods could not be used in all cases, but this should not seriously affect the results, as breakdown

TABLE 3
BREAKDOWN STRENGTH OF EBONITES MADE FROM VARIOUS RUBBERS

Rubber	Breakdown strength (kV (R.M.S.)/mm.)	Time taken to reach breakdown (sec.)
A	162	.105
	146	64
B	>140(a)	89
	>140(a)	55
C	>142(a)	82
	202	100
D	120	60
	170	68
E	104	36
	108	41
F	94	37
	168	73
G	(b)	(b)
	168	70
H	170	143
	146	58

(a) Punctured on side.
(b) Punctured immediately when raising voltage from about 5 kV.

strength varies little with vulcanization[7].   The British Standard method of test was used[8]; tests were made under oil, the voltage (50 cycles per second) being raised steadily until breakdown occurred (see Table 3).

Owing to the small number of replicate samples available and the consequent large error of measurement, the data in Table 3 show no significant differences between the rubbers.   These tests therefore do not demonstrate any improvement in breakdown strength from the use of the special raw rubbers, and thus do not bear out the statement of Nutthall[9], that by removing the proteins from latex by caustic alkali, the breakdown voltage of the resulting ebonite can be raised 300–400 per cent.

SURFACE RESISTIVITY BEFORE AND AFTER EXPOSURE TO LIGHT

The method used was that described already[10]. Most of the exposure tests were made with the mercury-vapor lamp, but some daylight exposures were made by placing the exposure boxes before an open window. The surface resistivity before exposure is given in Table 4. From curves of resistivity plotted against period of exposure, the periods required to reduce the resistivity to 10^{14} and 10^9 ohms were read, and are given in the taulated results (Table 5).

TABLE 4

APPARENT* SURFACE RESISTIVITY, BEFORE EXPOSURE, OF EBONITES MADE FROM VARIOUS RUBBERS

	Resistivity, ohms $\times 10^{18}$		
	Vulcanization		
Rubber	3 hrs.	5 hrs.	8 hrs.
A	—	1	—
B	—	3	>10; >10
C	3	10; >10; 2.5	1
D	>10	1; >10	>10; >10
E	—	0.25	3; >10
F	—	2; >10; 0.35	1
G	—	>10	—
H	0.5; >10	>10; >10; 0.15	1

* "Apparent" because volume current leakage may be a substantial part of the measured leakage.

TABLE 5

EXPOSURE PERIODS (HOURS)* REQUIRED TO BRING THE SURFACE RESISTIVITY DOWN TO 10^{14} OR 10^9 OHMS

	10^{14} ohms				10^9 ohms		
	Vulcanization				Vulcanization		
Rubber	3 hrs.	5 hrs.	8 hrs.		3 hrs.	5 hrs.	8 hrs.
A	—	4	—		—	12	—
B	—	$4\frac{1}{2}$	$4\frac{3}{4}$		—	14	$12\frac{1}{2}$
C	$4\frac{1}{2}$	$4\frac{3}{4}$ ($13\frac{1}{2}$)	5		$12\frac{3}{4}$	$12\frac{1}{4}$ (35)	11
D	5	$4\frac{1}{2}$	5 ($11\frac{1}{2}$)		$11\frac{1}{2}$	12	$12\frac{1}{2}$ ($28\frac{1}{2}$)
E	—	— (13)	$5\frac{3}{4}$		—	— (35)	$13\frac{3}{4}$
F	—	5 (13)	6		—	$13\frac{1}{2}$ ($32\frac{1}{2}$)	15
G	—	$5\frac{1}{2}$	—		—	14	—
H	$4\frac{1}{2}$	$4\frac{3}{4}$ ($14\frac{1}{2}$)	$6\frac{1}{2}$		$11\frac{1}{2}$	13 (38)	14

* Figures in brackets refer to daylight exposure and are expressed in standard hours[7]; the other figures relate to mercury-vapor lamp exposures.

The apparent initial resistivities (Table 4) are variable among tests on the same ebonite, doubtless owing to the difficulty of obtaining an absolutely clean surface. As, however, none of the specimens shows a value below 10^{17} ohms, it may be concluded that all the rubbers, including even the whole-latex rubber E, give ebonites that are satisfactorily free from surface leakage when tested on a freshly prepared surface. It is not possible to say that any one rubber gives better or worse surface resistivity than another.

Table 5 again shows no large differences between ebonites from different rubbers. As there is no evidence that the rate of surface deterioration varies with vulcanization, the values for the different vulcanizates may be pooled to reduce the experimental error. By so doing, and combining the 10^{14} and 10^9 ohm results, it is found that in the mercury-vapor lamp tests the range of variation in deterioration rate among ebonites made from the eight rubbers is only some 20 per cent; the daylight exposures indicate a similar variation.

As differences of this order have little practical significance, no real advantage, as regards light stability, is obtained by using the special rubbers. This is not surprising in view of the mechanism of surface deterioration, which is essentially a breakdown of the rubber-sulfur compound by the action of light, the breakdown products being then oxidized to sulfuric acid. It hardly seems likely that these processes would be substantially influenced by small amounts of such components as proteins, sugars, or mineral substances.

VOLUME RESISTIVITY

It is probable that in surface resistivity tests on freshly prepared specimens, current leakage takes place mainly through the body of the specimen rather than over the surface. Under these conditions, with specimens of the dimensions used, the volume resistivity is about one-twentieth of the apparent initial surface resistivity as given in Table 4. All the ebonites must thus have volume resistivities of at least 10^{16} ohms–cms., and often well above 10^{17} ohms–cms.

WATER ABSORPTION

Tests were made by exposing the finely rasped ebonite, previously dried, to an atmosphere of relative humidity 97 per cent at 20° C[11]. The initial absorptions, deduced as described above are given in Table 6. There was a very

TABLE 6

INITIAL WATER ABSORPTION IN PERCENTAGE BY VOLUME

Rubber	Vulcanization		
	3 hrs.	5 hrs.	8 hrs.
A	0.94	0.76	0.79
B	0.78	0.77	0.71
C	0.57	0.62	0.56
D	0.33	0.43	0.32
E	2.12	2.44	2.46
F	—	0.44	0.48
G	—	0.42	0.46
H	0.57	0.57	0.55
J	—	0.32	—
K	—	0.53	—

marked increase in absorption following the initial absorption in the case of J and K, which renders the initial absorption figures of doubtful value as indications of the water-absorbing capacity of these ebonites. This continued increase in water absorption may have some relation to the secular variation in electrical properties[12].

As there is no evidence that the water absorption varies with vulcanization[13] it is convenient to take the mean of the results for the three vulcanizing periods. In Table 7 these means are arranged in increasing order, the water absorptions for the corresponding raw rubbers being shown for comparison.

As would be expected, the ebonites made from the special rubbers (D, F, G, J and K) have the lowest absorptions. Of the other types, those which have been washed, *i.e.*, H (washed smoked sheet) and C (washed para), are the best; crepe (B) is rather better than smoked sheet, judged by the tests on the ebonites.

The raw rubbers do not show the same order of merit as the ebonites, although they fall into the same four groups, namely: D, F, G, J, K (low); H (medium); A, B, C (high); E (very high). If the extreme sample E is excluded, the correlation between the absorptions by the rubber and by the ebonite is not statistically significant. A possible reason for this is that the lengthy heating in presence of sulfur, involved in converting the rubber to ebonite, brings about chemical changes in the nonrubber components and so alters their water-absorbing capacity. The different components are affected to different extents, so that the effect of vulcanization varies according to the relative proportions of these components.

The conclusion is, therefore, that water absorption tests are a useful rough guide in distinguishing between good and bad rubbers, or in picking out those worthy of further investigation, but that if the rubber is intended for ebonite

TABLE 7

INITIAL WATER ABSORPTION IN PERCENTAGE

Rubber	Ebonite	Raw rubber
J	0.32	0.24
D	0.36	1.00
G	0.44	1.05
F	0.46	0.60
K	0.53	0.31
H	0.56	1.60
C	0.59	3.50
B	0.75	2.80
A	0.83	1.75
E	2.34	10.0

manufacture the information should be supplemented by absorption tests on the ebonites themselves. A similar conclusion was reached in relation to the use of purified rubber in making soft vulcanizates[14].

CORRELATIONS BETWEEN ELECTRICAL PROPERTIES, WATER ABSORPTION, AND ASH

In Table 8 the ebonites are arranged in order of increasing loss factor (permittivity $\times$ power factor), and the corresponding initial absorption figures for the ebonite and raw rubber and ash figures for the ebonite are given.

There are obvious signs of parallelism between the loss factor and water absorption of the ebonite, since both properties divide the materials into the same four groups; (1) G, F, D, J, K; (2) H; (3) B, A, C; (4) E. If the extreme sample E is excluded the correlation between loss factor and water absorption is just significant at the 5 per cent level. Somewhat unexpectedly, the absorption by the raw rubber shows a still closer correlation with loss factor.

Taking the results as a whole, the electrical properties of ebonite, tested in the normal condition, show some relation to its water-absorbing capacity and that of the raw rubber used, low absorption corresponding to low loss factor, but small differences in water absorption are not necessarily accompanied by corresponding differences in loss factor.

Low water absorption would be expected to result in reduced sensitiveness of electrical properties to changes in ambient humidity, and as already noted[12], the ebonites having low absorption (D, F, G, H, J and K) do show less increase in permittivity on exposure to a high humidity.   The power factor shows a similar but not so definite tendency; the low-absorption ebonites, D, F and G, increase by 0.004–0.05 at the high humidity, compared with 0.07–0.10 for the more absorptive ebonites from smoked sheet (A) and para (C), but the washed smoked sheet ebonite H shows a larger increase (0.12) than the crepe ebonite B (0.03) in spite of its lower absorption; with the low-absorption ebonites J and K, the true humidity effect seems to be masked by the secular change.

The differences between the various ebonites (excluding E) as regards moisture stability, however, are not large; thus the percentage difference between the loss factors at 90 per cent relative humidity and 75 per cent relative humidity amounts to some 10 per cent for the ebonites made from ordinary rubbers (A, B, and C), compared with 5 per cent for those showing the greatest stability to humidity changes, namely: D, F, G, and H.

TABLE 8

Rubber	Loss factor	Water absorption (%)		Ash (%)
		Ebonite	Rubber	
J*	2.20	0.32	0.24	0.46
K*	2.29	0.53	0.31	0.49
G	2.41	0.44	1.05	0.36
F	2.57	0.46	0.60	0.52
D	2.74	0.36	1.00	0.35
H	2.94	0.56	1.60	0.25
B	3.10	0.75	2.80	0.33
A	3.15	0.83	1.75	0.45
C	3.30	0.59	3.50	0.33
E	7.1	2.34	10.0	0.78

* Initial values for loss factor have been used to avoid complications due to the pronounced secular change; loss factors after final conditioning at 75 per cent relative humidity are 2.68 and 2.92, respectively.

Table 8 shows that with the exception of E no correlation exists between the ash of the ebonite and its loss factor.   This is not surprising, because the mineral ingredients must differ in nature and hence in solubility in water, degree of ionization, and the mobility of the ions, and radical changes occur during incineration.   Moreover, water-soluble or water-absorbent organic substances might have a marked influence.

SUMMARY

Tests have been made on unloaded ebonites prepared from ordinary commercial types of natural rubber, special (deproteinized) rubbers having reduced contents of protein and(or) other water-absorbent substances, and a whole-latex rubber containing relatively large percentages of these substances, to determine to what extent these substances influence the electrical properties of the ebonite and, hence, whether any technically useful improvement can be effected by using specially prepared rubbers.

Permittivity and power factor at 10^6 cycles per second, but particularly power factor, are somewhat improved by using the special rubbers, so that the dielectric loss can be reduced by about 30 per cent.   In addition, the increase in dielectric loss caused by exposure to high humidity or by a rise of tempera-

ture is in general lessened by the use of these rubbers. Similar, though smaller, improvements in the properties of the ebonite are obtained by washing ordinary commercial rubber (smoked sheet).

Although a definite improvement in dielectric loss is obtained, it does not seem probable that purification of natural rubber would lead to ebonites with dielectric properties approaching those of polystyrene, for instance. It seems unlikely that even complete elimination of the water-absorbent impurities would reduce the dielectric loss by more than 50 per cent; the rubber-sulfur compound itself thus appears to be responsible for a fair proportion of the loss normally observed.

The large percentages of water-soluble substances present in whole-latex rubber increase the permittivity and especially the power factor of the ebonite made from it.

The dielectric properties of ebonite are related, though not closely, to its water-absorbing capacity and that of the raw rubber used, low absorption being in general accompanied by low dielectric loss and reduced sensitiveness to humidity variations. There is only a rough parallelism between the water absorptions of raw rubbers and the corresponding ebonites. Probable reasons for this are indicated. It is concluded that water absorption tests on raw rubber form a useful, though only approximate, guide to its value for making electrical ebonite; electrical tests on the ebonite must be the final criterion.

Apart from very impure whole-latex rubber, no correlation can be traced between the inorganic content (ash) of ebonite and its electrical properties. The probable reason for this is indicated.

There is evidence that the dielectric loss of ebonite may increase with the passage of time. In view of its obvious theoretical and practical importance, this phenomenon requires further study.

No technically useful advantage as regards breakdown strength, volume resistivity, surface resistivity, or stability to light, by the use of the special rubbers, is evident in the present work.

The plastic yield characteristics of ebonite are not appreciably altered by using special rubbers.

Estimations of uncombined sulfur and also plastic yield tests show that one of the deproteinized rubbers vulcanizes more rapidly than the rest, which differ little among themselves.

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BEHAVIOR OF RAYON TIRE CORD DURING
LATEX DIPPING *

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The large scale usage of GR-S has markedly accelerated the trend to the use of rayon cord in tires. During 1946, rayon constituted approximately 40 per cent of the more than 500,000,000 pounds of tire fabrics produced. Lack of supply limited further usage.

The factors behind this change are involved, but most outstanding is the heat problem. Built into a tire, GR-S generates more heat than rubber on flexing. Moreover, there is a significant loss in physical properties of GR-S at elevated temperatures. Rayon cord fits into this problem because at equal tensile strength it has a lower gage than conventional cotton constructions. This is the prime force behind the trend to rayon, for it enables thinner tires to be built. In turn, the thinner tire body generates less heat, and at the same time it allows this heat to be more easily dissipated.

The use of rayon in tire fabrication presents a problem. Before use, the rayon must be treated with an adhesive so that it will bond to rubber sufficiently to prevent ply separation of the tire in service. The necessity for this pretreatment reveals the essential difference between rayon and cotton; the latter needs no special adhesive, although many treatments may be used to good advantage.

Chemically, rayon and cotton are both essentially cellulose and one would expect them to exhibit similar specific adhesion to rubber. Blow and Knight[1] explain that the unexpected differences in the bonding strengths of cotton and rayon to rubber are due to the diverse chemical nature of the oil or waxy surface finish. But they are alone in this opinion. The more popular concept, expressed by Scholes[2], is that bonding is purely mechanical. Cotton cord has a fuzzy surface which is due in part to a convoluted fiber, but primarily to the protruding ends of the staples. This fuzz anchors the cotton by becoming embedded in the rubber. On the other hand, rayon tire cord is a smooth-walled fiber and presents no fuzz from fiber ends because of its continuous filament construction. Added weight is given to this latter concept of mechanical adhesion by a report[3] on the manufacture of German rubber goods, wherein spun rayon required no special adhesive treatment.

There is an extensive literature coverage of adhesives for rayon, especially patents[4], and considerable discussion of the dipping process for cotton[5], but the authors have been unable to find any published information regarding the overall process of rayon dipping.

While dipping rayon cord, the authors observed a surprising change in the latex bath concentration, a phenomenon that does not occur with cotton (Fig-
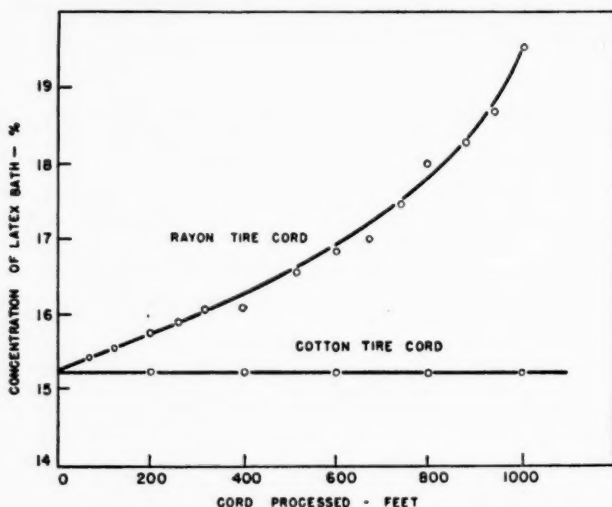
FIG. 1.—Effect of cord type on latex bath concentration.

ure 1).   This anomalous behavior suggests that additional data are required concerning the behavior of rayon during dipping.

In this work, undertaken to obtain information for controlling plant dipping processes, it was found, Figure 2, not only that rayon differs from cotton, but
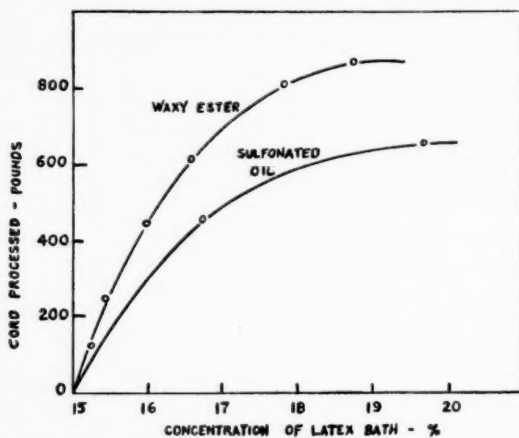
FIG. 2.—Relation between amount of cord dipped and amount of bath used in production run.

that rayons of different manufacture vary among themselves.   The nature of these differences is discussed.   They center largely about the fiber lubricant used as a finishing agent in rayon manufacture.

MATERIALS AND EQUIPMENT

Table I gives information on the cords and latices used in this study.   Additional information regarding latices for cord treatment has recently been pub-

TABLE I

MATERIALS USED

	Cord A	Cord B
No. of filaments	480	480
Size	1100/2	1100/2
Construction	Z/S^2	Z/S^2
Ply	11.40	11.00
Yarn	13.83	15.39
Tensile strength (lb.) oven dry	19.16	18.35
Stretch (10 lb.) oven dry	5.26	4.10
Gage	0.024	0.025
Yds. per lb. at 12% moisture regain	1835	1812
Manufactured from	Wood pulp	Cotton linters
Finishing agent	Waxy fat ester	Sulfonated oil
Wetting-out time (sec.)	167	11

Latices.

(1) GR-S latex type 3, from U. S. Rubber Co., Torrance, Calif.

(2) Whole tire reclaim dispersion with approximately 9% casein.

lished[6]. In Table I it is shown that the two cords are practically identical in construction and physical properties. Of major difference, however, are their wetting-out characteristics, 11 and 167 seconds, respectively. This difference may be attributed to the associated finishing agents.

The fast wetting-out cord is finished with a sulfonated oil, whereas the other is finished with a waxy fat ester. Although the nature of the surface finish has been previously discounted as being significant in specific adhesion, it is here introduced as governing the speed of wetting-out, a property of basic importance in latex dipping. This characteristic largely explains the differ-
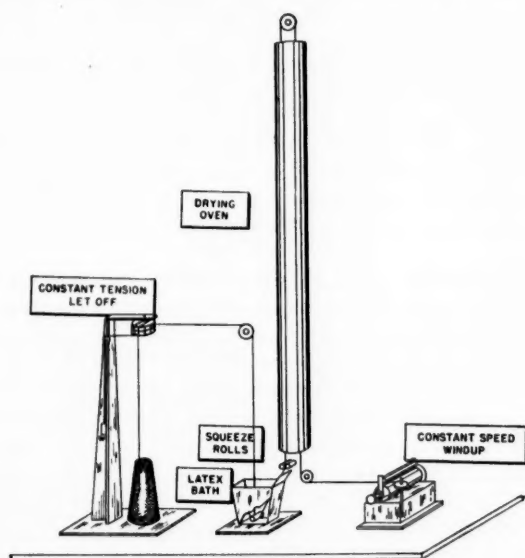
FIG. 3.—Laboratory cord dipping unit.

Tension varied by changing weight; speed changed by varying diameter of roll or cog; contact time changed by varying depth of liquid.

ences herein reported.   (As a reference point, cotton tire cord has an indefinite wetting-out time under conditions of the test used.)

Table I further reveals that cord *A* is manufactured from wood pulp, whereas cord *B* is manufactured from cotton linters.   This detail, however, was found to be unimportant; after extraction of the finishing agent with a solvent, the cords behaved identically in the dipping process.

For rayon adhesive treatment, two-phase systems have been generally employed.   The first phase consists of a water suspension of rubber, either a reclaim dispersion or a synthetic or natural latex, to obtain a bond to the polymer; the second phase consists of a particular rayon adhesive which may be either a protein material, such as casein, or a synthetic resorcinol-formaldehyde resin former.   A blend of GR-S latex and reclaim dispersion containing casein was used in the work described in this paper.

All testing was done on a small scale laboratory unit (shown in Figure 3) which was designed to permit independent control and measurement of all essential variables.   A single cord was dipped in a continuous process, similar to the factory method.

For simplicity, cords *A* and *B* are hereafter referred to by their respective finishing agents—namely, waxy ester and sulfonated oil.

EFFECT OF CORD ON LATEX BATH

As shown in Figure 1, the dipping of cotton tire cord results in no significant bath changes.   On the other hand, observations made during the continuous dipping of rayon showed changes sufficient to require control measures.   Some of the details of how the cord affects the bath are as follows:

Concentration.—It was found that the concentration of the latex bath increased when either the sulfonated oil or the waxy ester cord was dipped. Tables II and III show, however, that a marked difference exists between the two cords.   This difference is more fully demonstrated in Figures 4 and 5, which show the concentration change when the basis for comparison is either the cord dipped or the solids pickup.   An explanation for the reversal in magnitude on the two bases is given in Figure 6.   Approximately 3.4 times more waxy ester cord than sulfonated oil cord may be dipped for a given weight of solution consumed; or stated in another way, sulfonated oil cord has approximately a threefold higher wet pickup.   As discussed under Machine Operation Variables, the wet pickup may be adjusted for the two cords by squeeze roll pressure.

Absorption characteristics.—To obtain a better understanding of underlying relations, it is necessary to reduce the above concepts to a more fundamental basis—that is, to determine the ratio of water-to-solids pickup for each cord, irrespective of the differences in total wet pickup.   It is also desirable to know whether this ratio is constant or depends on the bath concentration.

It was found, surprisingly enough, that the ratio of water-to-solids pickup of both cords was identical for all concentrations of the bath examined.   Moreover, it was found that the ratio of water-to-solids pickup decreases as the concentration of the bath increases.   This relationship is illustrated by equations obtained through a statistical treatment, by the least squares method[7], of data in Tables II and III.

$$Y = 0.4X + 2.2 \text{ waxy ester cord}$$
$$Y = 0.4X + 2.1 \text{ sulfonated oil cord}$$

TABLE II
INFLUENCE OF WAXY ESTER CORD ON LATEX BATH

Increments cord-dipped (grams)	Wet pickup (grams)	Bath concn. (%)	Solids pickup (%)	Water-to-Solids	
				Pickup by cord (X)	In bath (Y)
0	..	15.1	..	..	5.62
10	6.2	15.2	7.3	7.49	5.58
10	7.3	15.5	7.4	8.86	5.45
10	6.9	15.7	7.8	7.85	5.37
10	7.0	16.2	8.5	7.23	5.17
10	7.0	16.3	8.4	7.32	5.13
10	7.1	16.5	8.0	6.98	5.06
10	7.0	16.7	8.5	8.29	4.99
10	7.8	16.5	8.6	8.07	5.06
10	6.3	16.8	8.0	6.08	4.94
10	7.5	19.9ᵃ	..	..	..
10	7.4	17.4	9.6	6.71	4.75
10	7.5	17.6	9.9	6.58	4.68
10	7.4	17.8	10.8	6.76	4.62
10	7.2	18.1	10.8	5.67	4.52
10	8.7	18.7	12.2	6.13	4.35
10	7.6	18.7	11.8	6.27	4.35
10	9.9	19.3	14.2	5.97	4.18
10	10.4	19.7	16.5	5.30	4.08
10	10.9	20.5	16.7	4.03	3.88

ᵃ Discarded as obvious error.

TABLE III
INFLUENCE OF SULFONATED OIL CORD ON LATEX BATH

(Operating conditions: tension, 50 grams; speed, 90 in. per min.; wiping action, none; contact time, 5 sec.   Latex bath: reclaim dispersion—GR-S latex blend with cure)

Increments cord-dipped (grams)	Wet pickup (grams)	Bath concn. (%)	Solids pickup (%)	Water-to-Solids	
				Pickup by cord (X)	In bath (Y)
0	..	15.1	..	..	5.62
5	10.0	15.4	24.7	7.11	5.49
5	12.6	15.5	26.8	8.40	5.45
5	11.2	15.7	27.3	7.14	5.37
5	12.9	15.9	27.0	8.54	5.28
5	12.2	16.1	27.3	7.95	5.21
5	10.5	16.0	26.7	6.96	5.24
5	11.1	16.4	27.5	7.07	5.08
5	11.6	16.5	31.6	6.33	5.06
5	11.3	16.8	27.8	6.16	4.95
5	10.7	17.0	29.7	6.21	4.88
5	11.3	17.4	29.2	6.73	4.74
5	11.4	18.0	31.6	6.22	4.56
5	11.5	18.3	29.7	6.67	4.46
5	11.9	18.6	35.4	5.66	4.37
5	11.4	19.6	34.4	5.63	4.11

where Y = ratio of water-to-solids in latex batch, and X = ratio of water-to-solids pickup by cord.

No theoretical implication should be attached to the linear relation expressed by these equations, as they merely describe one good fit of the data in the range examined.   Nevertheless, there is a very high degree of correlation between the two variates as the correlation coefficient, when tested statistically for significance by the t test, is beyond the 1 per cent level[7].
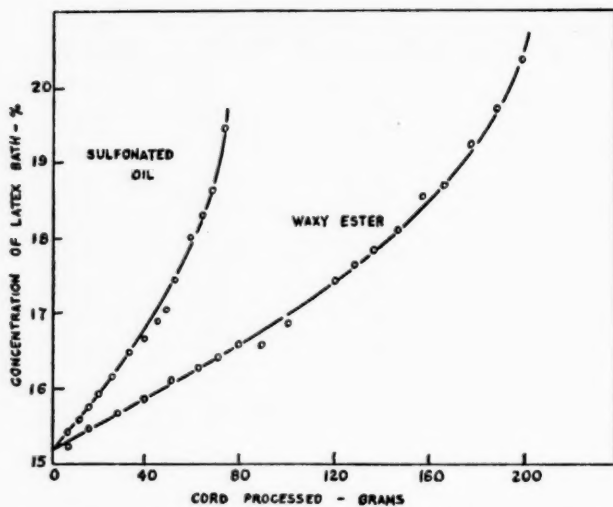
FIG. 4.—Effect of weight of cord dipped on latex bath concentration.

These data indicate clearly that some factor or factors common to both cords are operative, causing selective absorption of the water component.

The most plausible interpretation of this selective absorption is that the cord acts as a filter allowing water to flow into the interior but offering resistance to the passage of the relatively large latex particles. Bongrand[8] and Stevens and Stevens[9] point this out for cotton; Fischer[10] uses this phenomenon as a basis for patent rights.

The assumption of a filtering process offers an explanation for the difference in the action of rayon and cotton on the bath. It has been shown above that
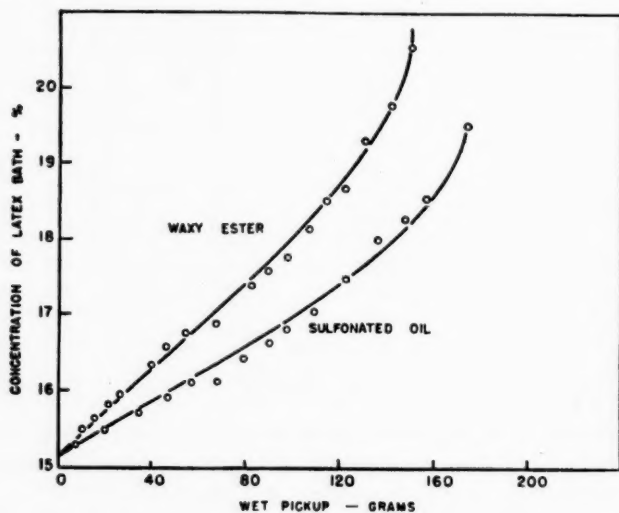
FIG. 5.—Change in bath concentration against weight of bath used.

both types of rayon under consideration wet out, or sink in water, in a matter of seconds, whereas cotton floats indefinitely on the surface. Furthermore, it has been shown[11] that on thoroughly soaking in water, rayon swells approximately twice as much as cotton. It would, therefore, be reasonable to assume that during the momentary (5 seconds) submergence in water used in cord dipping, swelling of cotton is negligible; rayon swells to a marked degree. This allows rayon to imbibe liquid from the bath, and hence increases its concentration.

Condition of auxiliary materials.—The water component has been shown to be selectively absorbed from the latex. A question then arises as to the status of the other components of the bath. Of importance are the casein used to obtain adhesion and the bath stabilizers such as soaps, wetting agents, etc. Apparently, casein does not migrate with the water as shown by a constant Kjeldahl nitrogen content of the bath during processing.
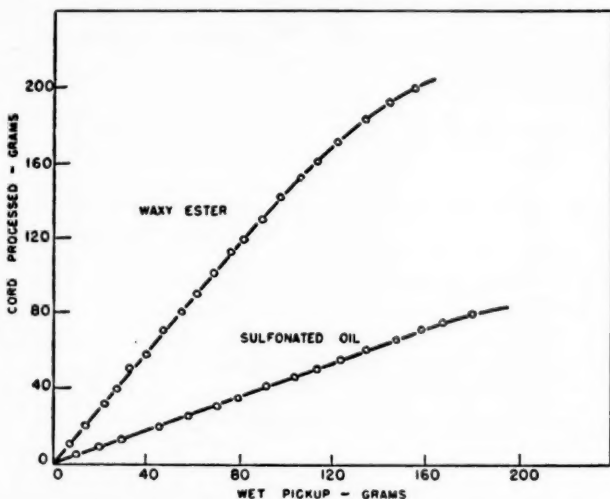
FIG. 6.—Relation between amount of cord dipped and amount of bath used.

Wetting agents appeared to follow a similar pattern, for no change could be observed in surface tension during processing. These results, therefore, do not support Fischer's[12] findings that cotton batting preferentially sorbs surface-active materials from natural latex, and causes a gradual increase in surface tension of the bath. No explanation is offered except to point out that his work was performed under batch dipping conditions. This investigation was conducted under continuous dipping conditions.

CORD ADHESION

The primary purpose of treating rayon tire cord with latices is to obtain sufficient adhesion to rubber stocks to prevent ply separation in tires. It is obvious that the bond strength obtained from a cord treatment depends on the nature of the adhesive as well as on the amount applied. The nature of rayon adhesives is beyond the scope of this work. The results reported here are then concerned only with bond strength as it relates to the quantity of adhesive material deposited on the cord.

Evidence presented in Table IV emphasizes the dependence of adhesion on the amount of adhesive coating on the cord, or, stated in the terminology used in this paper, on the solids pickup. Adhesion values in Table IV are expressed in pounds as measured by the H test[13] which is the force necessary to pull a single cord out of a block of rubber in which it had been vulcanized. A lower limit of 12 pounds has generally been found to be acceptable for tires. Staple rayon meets this minimum without any treatment. Cotton tire cord also meets the above limit without any dipping treatment. In contrast, as shown in Table IV, untreated continuous filament rayon has an adhesion value of less than 8 pounds. The assumption that the poor adhesion of continuous filament rayon to rubber is due to the smoothness of the cord is thus well supported, and emphasizes the necessity of ensuring adequately deposited solids during dipping.

TABLE IV

INFLUENCE OF SOLIDS PICKUP ON ADHESION
(H TEST)

(Operating conditions: tension, 50 grams; speed, 66.5 in. per min.; wiping action, none; contact time, 5 sec. Latex bath: reclaim dispersion—GR-S latex blend with cure)

Waxy ester cord		Sulfonated oil cord		Staple cord sulfonated oil	
Solids pickup (%)	Adhesion[a] (lb.)	Solids pickup (%)	Adhesion[a] (lb.)	Solids pickup (%)	Adhesion[a] (lb.)
0	7.5	0	7.6	0	14.2
0.4	7.8	1.7	9.0	4.8	17.6
0.5	8.0	2.6	10.6	26.0	20.5
0.8	8.1	3.9	10.9	..	..
1.2	9.4	6.1	12.2	..	..
1.9	10.9	8.4	13.8	..	..
2.5	11.0	9.5	14.1	..	..
5.9	12.0	22.0	17.4	..	..
9.9	13.4	46.3	19.8[b]	..	..
21.1	14.8	..	..	..	..

[a] Average adhesion for two sets of data, ten tests each.
[b] Cord broke in practically all cases.

SOLIDS PICKUP

The factors in dipping that affect solids pickup may be grouped into cord, latex bath, and machine operation variables.

CORD VARIABLES

Specific properties of the cord which need to be considered are fuzziness, wetting-our, and construction.

Fuzziness.—It would be expected that a cord with many capillary side wicks (fuzzy) would tend to pick up more latex solids than a relatively smooth, slick cord. This assumption is borne out in Table V, which points out a three-fold difference in solids pickup of cords of similar manufacture but differing principally in fuzziness—sulfonated oil continuous filament cord and sulfonated oil staple cord.

Wetting-out.—A major point in the discussion thus far has been the behavior difference of sulfonated oil and waxy ester cords caused in turn by their differing wetting-out time. Table V adds further evidence by showing a several fold increase in solids pickup of sulfonated oil over waxy ester cord over a wide range of bath concentrations.

TABLE V

SOLIDS PICKUP AT VARIOUS CONCENTRATIONS OF LATEX BATH

(Operating conditions: tension, 50 grams; speed, 66.5 in. per min.; wiping action, none; contact time, 5 sec. Latex bath: reclaim dispersion—GR-S latex blend with cure)

Bath concn. (%)	Viscosity, 25° C (cp.)	Solids pickup on cord (%)		
		Waxy ester	Sulfonated oil	Staple sulfonated oil
5	1.67	0.4	1.7	4.8
7.5	1.94	0.5	2.6	..
10.0	2.46	0.8	3.9	..
12.5	3.53	1.2	6.1	..
15.0	8.36	1.9	8.4	27.3
17.5	26.1	2.5	9.5	..
20.0	57.2	5.9	22.0	..
22.5	83.5	21.1	46.3	..

Construction.—The construction of tire cord is essentially stabilized, and samples for dipping which would not introduce other variables at the same time were not available to the authors.   Nevertheless, as a summation of experience with a wide variety of cord constructions a general rule may be expressed that a tighter twist tends to favor less pickup of solids.

LATEX VARIABLES

Of interest in solids pickup are the following four properties which lend themselves to production control.

Concentration.—As demonstrated in Figure 1, the concentration of the bath increases as rayon cord is processed.   Unless concentration is held constant by the addition of water, the solids pickup increases, as shown in Table V. This not only changes adhesion, but causes deviation in square yard weights going to the calender.   Although concentration may be regulated, it has upper and lower boundaries.   A concentration above the upper limit results in an unworkable solution viscosity, and dilution below the lower limit results in flocculation of most latex systems.

Viscosity.—A theoretical analysis would lead one to believe that solids pickup depends on viscosity, as the latter property influences drainage characteristics, and to some extent flow of latex into the interstices of the cord. These interstices may be considered capillaries[14] and any liquid filling them follows the laws of capillary flow[15].

To observe the validity of these statements, a series of latex solutions at constant percentage of solids was prepared, with the addition of minute amounts of methylcellulose thickener.   A range of viscosities from 1 to 50 cp. was obtained.   The dependence of solids pickup on viscosity is shown in Figure 7.

An exact relation between solids pickup and viscosity of rayon dipping solutions is difficult to obtain because latices containing thickeners, such as casein, exhibit thixotropy.   Also, there probably is a subsequent local decrease in viscosity around the cord as it passes through the latex; this is caused by the shearing action, which disrupts the liquid structure.   Madge[14] points out this effect in producing dipped articles where the rate of withdrawal affects the weight of the deposit.

Particle size.—It has been stated[16] that a latex with a small particle size, such as GR-S, impregnates textiles more readily than a latex, such as Hevea, with a relatively large particle size.   An attempt was made to determine indirectly whether particle size had a bearing by noting its effect on solids

pickup; the assumption was made that the latex which penetrated deeper would result in a higher solids pickup. It was found that the solids pickup for natural latex and GR-S are approximately equivalent, even though natural latex has a particle size approximately 10 times that of GR-S[17]. Although this evidence would indicate that no difference in impregnation is due to particle size, additional evidence on this point is still required.

Surface tension.—It is generally assumed that solids pickup and penetration increase as the surface tension decreases. It was found in this work that solids pickup by waxy ester cord is not influenced by surface tension, and that sulfonated oil cord has only a slight increase at or below 46 dynes per cm. This evidence was obtained by varying surface tension of GR-S latex through the addition of Aquarex-D (E. I. du Pont de Nemours & Co.). An explanation for the difference between the cords may well be that the waxy finish on the
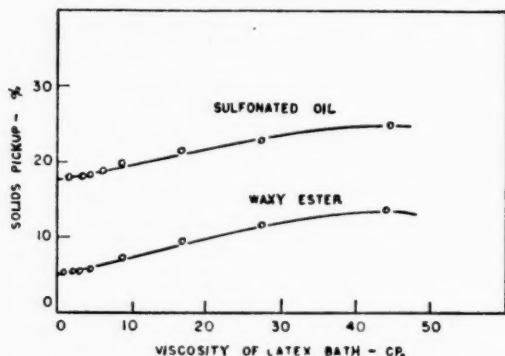
Fig. 7.—Effect of viscosity of latex bath on solids pickup.

former cord does not allow thorough wetting out regardless of the surface tension, particularly because the contact period of cord with latex was only 5 seconds. However, this time was chosen as approximating the contact period in production dipping machines.

Nederveen[18] in a microscopic study found with cotton that mixing wetting agents with latex causes only very slight penetration of rubber between the fibers of the yarn.

MACHINE OPERATION VARIABLES

Modern dipping units allow considerable flexibility in determining solids pickup. They are designed to regulate independently the important characteristics of cord tension, speed, wiping action, and contact time. Results obtained on the laboratory unit were as follows:

Cord tension through bath.—The data plotted in Figure 8 show a rapid drop in solids pickup with tension up to values in the neighborhood of 100 grams per cord. Beyond this figure, the dependence on tension begins to level out. The role of tension is as expected, because it limits swelling and restricts the size of the interstices.

Dipping speed.—As demonstrated in Figure 9, solids pickup is a direct function of speed, at least in the range examined. Although the upper limit of this study was approximately only one-tenth the speed of factory dipping units, it is believed that the trend is valid, for the dependence on speed is
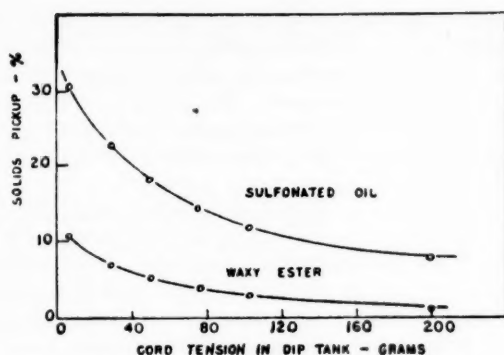
FIG. 8.—Effect of cord tension in dip tank on solids pickup.

probably a matter of drainage. In turn, drainage is influenced by factors previously discussed including cord construction, fuzziness, wetting-out, viscosity, and surface tension.

Wiping action.—Increased wiping action, such as obtained by the use of squeeze rolls, results in lower solids pickup. No data are shown because the difficulties of designing experimental squeeze rolls with controllable pressure have not yet been worked out. However, plant experience has shown that solids pickup may be varied over a wide range by adjusting squeeze roll pressure.

An interesting speculation is posed by the practice of regulating solids pickup by varying the dip solution concentration simultaneously with squeeze-roll pressure. Common dipping practice in the impregnation of textiles with resins for fabric stabilization is to use substantial squeeze roll pressure for removing excess resin. It has been postulated that this pressure also compresses the fabric, which then expands after passage through rolls and tends to suck the resin into the interior, much as a sponge; this leaves the surface relatively free of resin. Whether a similar phenomenon is operating in latex dipping is not known, but it suggests a fruitful field of investigation.
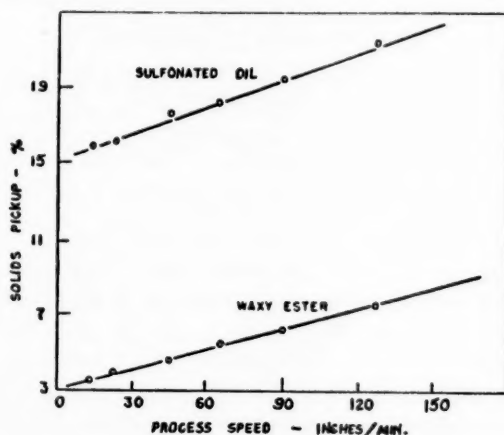
FIG. 9.—Influence of processing speed on solids pickup.

Contact time.—Contact time of cord and latex on production units varies according to the machine speed and liquid level in the dip tank. In this work, however, even after repeated testing, no valid relation between contact time and solids pickup could be established. Nevertheless, the data collected show that some factor or factors were operative that could not be attributed to the variations in testing. Apparently, this problem is more complex than it appears on the surface.

The authors' investigation, therefore, did not corroborate the work of Nederveen[18], who found, with cotton cords, that prolonging the contact period with latex causes the total amount of rubber taken up to be lower than when the thread travels more rapidly and the contact time is shorter. Nederveen, however, decreased the contact time by increasing the speed of processing, which, as previously pointed out, markedly influences solids pickup. Undoubtedly, his results represent primarily the influence of speed rather than that of contact time.

TESTING METHODS

Surface tension was determined by the drop-weight method, using a standard stalagmometer.

Viscosity was measured on the Stormer instrument at 25° C.

Wetting-out time was determined by dropping a 2-inch length of the cord on the surface of the liquid and noting time in seconds for the cord to submerge.

Nitrogen was determined by the Kjeldahl method, using aniline as a control.

Adhesion was tested according to the *H* method, using a natural rubber zinc carcass stock.

Solids pickup was computed as the weight of solid material pickup by the cord expressed as a percentage of the oven-dry weight of the raw cord.

$$\% \text{ solids pickup} = \frac{(\text{wt. of dry treated cord}) - (\text{wt. of dry raw cord})}{(\text{wt. of dry raw cord})} \times 100$$

Eighty feet of treated cord were measured, oven-dried, and weighed. Raw cord was treated with water, oven-dried, and weighed as a control.

SIGNIFICANCE OF RESULTS

The experimental observations report only quantitative differences between two grades of rayon employing two different finishing agents. The data in no way indicate the relative merit or desirability of any one type. Emphasis is placed on the fact that if the two grades are used interchangeably in factory dipping operations without concurrent modification of operating procedures, variations in solids pickup, adhesion, and square yard weight to the calender result. Each tire plant must determine for itself whether these differences are significant in terms of its own processes. As to performance, it is known that very successful tires have been built from all grades of rayon.

SUMMARY

A study of the behavior of two types of rayon tire cord during latex dipping was made with a laboratory treating unit. Results of the tests showed certain facts.

The concentration of the latex bath increased as rayon tire cord was dipped. No change occurred in dipping cotton.

Based on the weight of cord dipped, sulfonated oil cord caused a higher increase in bath concentration than waxy ester cord; based on the weight of latex consumed, the order was reversed.

Waxy ester cord had relatively slow wetting-out characteristics compared to sulfonated oil cord; compared to both, cotton is infinitely slow.

The ratio of water-to-solids pickup with both cords is identical for all concentrations of the bath examined. Because of this characteristic both cords behave identically in the bath provided the squeeze rolls are adjusted to give equal solids pickup.

Ratio of water-to-solids pickup decreases as the concentration of the bath increases.

Stable fibers, both cotton and rayon, need no adhesive treatment for satisfactory bonding to rubber. In contrast, continuous filament rayon cannot be used until it is treated.

Adhesion is a function of solids pickup.

Sulfonated oil cord picks up two to four times as much solids as waxy ester cord under a variety of conditions because of better wetting-out properties. By changing either the squeeze-roll pressure or the bath concentration solids pickup is changed.

Cord produced from staple rayon picks up more solids than continuous filament cord because of protruding fiber ends.

An increase in concentration of the latex bath causes an increase in solids pickup. Viscosity acts similarly.

Particle size has no appreciable effect on solids pickup.

Surface tension does not affect solids pickup by waxy ester cord; it does affect sulfonated oil cord to a minor degree at or below 46 dynes per cm.

An increase in cord tension through the latex bath decreases solids pickup.

As the speed of processing is increased, solids pickup increases.

A wiping action on the dipped cord decreases solids pickup.

No relation between contact time and solids pickup could be established.

ACKNOWLEDGMENT

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DETERMINATION OF RESISTANCE TO ABRASIVE WEAR*. VIII. INFLUENCE OF SOFTENERS IN TESTS WITH THE AKRON-CROYDON AND DU PONT MACHINES

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INTRODUCTION

It was noticed, when testing some commercial tire tread rubbers on the du Pont machine, that the abrasion resistance varied considerably from one rubber to another in spite of the fact that they were closely similar in stress-strain properties. From a study of the composition of the mixings it appeared that the softeners were responsible for the observed differences in abrasion resistance.

Tests on the same stocks with the Akron-Croydon abrasion machine showed generally similar, but much smaller, differences in abrasion loss.

It has previously been pointed out[1] that increasing the quantity of stearic acid in a tire tread mixing results in low abrasion losses on the du Pont machine. Moreover, a comparison of the behavior of pine tar and mineral rubber as softeners showed that these can affect abrasion resistance as measured by the du Pont machine in a manner inexplicable by the usual theories regarding the action of softeners in vulcanized rubber[2]. With mixings containing 8 parts of stearic acid, low results were obtained on an Akron machine[2].

In view of these published results and those obtained on the commercial tire tread stocks referred to above, it was decided to investigate the effects of two softeners on the abrasion resistance of tread rubbers as measured by the Akron-Croydon and du Pont machines. It was thus hoped to be able to determine (1) whether the effects of the softeners depend on the type of abrasion machine used, and (2) how the effects depend on the nature and the amount of softener.

EXPERIMENTAL

In the first series of tests the following mixing was used as the base stock to which softeners were added: Smoked sheet, 100, sulfur 3, MPC black 45, zinc oxide 8, mercaptobenzothiazole 1. Stearic acid and pine tar were chosen as the softeners, since they are the most widely used in tire tread mixings.

The mixing was carried out in the following manner. An MPC black master-batch (55:45 rubber-black), smoked sheet, zinc oxide, and mercaptobenzothiazole were first mixed together. The batch was then divided into four equal parts and the requisite softener or softeners (see Table 1) were added to each part, followed by the sulfur. The period of mixing and conditions for

TABLE 1

Softener, and parts by weight per 100 parts of rubber	Akron machine, abrasion loss (cc.)	Du Pont machine		
		Abrasion loss		Energy used (H.P.)
		cc. per hr.	cc. per H.P.-hr.	
Stearic acid, 3	0.189	2.94	147	0.0200
Stearic acid, 6	0.175	2.31	122	0.0189
Stearic acid, 1; pine tar 2	0.189	7.5*	330*	0.0225*
Stearic acid, 1; pine tar 5	0.150	6.2	300	0.0205

* This rubber gave very variable results; the figures quoted appear to be the most probable values.

the addition of softener and sulfur were as nearly as possible the same for each mixing. By proceeding in this way, it was hoped that any differences in dispersion of the black due to the different softeners would be minimized.

Molded abrasion specimens were prepared from each mixing by vulcanizing for 30 minutes at 148° C, the filled molds being kept in the press for 5 minutes at this temperature before applying the mechanical pressure.

The conditions of test were as follows.

Akron-Croydon machine.—Angle of inclination of specimen 15°; load on specimen 10 lb.; speed of rotation of specimen 60 r.p.m.; abrasive wheel No. 36 grit hard fused alumina (Grade P); preliminary run 1,000 revolutions of abrasive wheel, weighings then taken after 5 successive runs of 500 revolutions each; result quoted as mean volume loss (cc.) per 1,000 revolutions of abrasive wheel. Two specimens were tested, and the average result is quoted.

Du Pont machine.—Emery paper No. 0 of H. L. Scott Co.; total load on specimens 8 lbs.; duration of test-run 20 minutes after a preliminary run until the samples seated evenly; air blast for cleaning abrasive 25 lb. per sq. in.; abrasion loss quoted (1) as cc. per hr., (2) as cc. per horse-power-hr. Three tests were made, each on a different pair of specimens, and the average of the results is quoted. Results are given in Table 1.

According to these results the amount and especially the nature of the softener can have a considerable influence on abrasion loss as measured by the du Pont machine, whereas the Akron-Croydon machine does not show anything like such large differences

It was thought that these results might be open to criticism on the ground that the accelerator used is to some extent dependent on stearic acid or other organic acid for its activity. The work was therefore repeated, using a different accelerator which does not depend for its efficiency on stearic or other acid. It was thus possible to omit stearic acid entirely from the pine tar mixings, thus giving a better comparison between the two softeners. The base stock used was: smoked sheet 100, sulfur 3, MPC black 45, zinc oxide 5, diphenyl-guanidine 1.

The mixing procedure was the same as for the previous set of mixings. The vulcanizing conditions for the abrasion specimens were likewise the same as before except that a higher temperature was used (153° C).

With these mixings, also, sheets 6 × 6 × 0.1 inch were vulcanized for 30 and 35 minutes at 153° C for making tensile tests. These tests were made with standard dumb-bell specimens (1 × ¼ inch test length; 1¼ inch wide ends) on the Scott machine (see Table 2). Thus the effects of the softeners on the stress-strain properties could be compared with their effects on abrasion resistance.

TABLE 2

Softener, and parts by weight per 100 parts of rubber	Vulcanization (min.)	TS	M100	M300	M500	EB
Stearic acid 3	30	3260	225	1330	3035	520
	35	3090	235	1310	3090	500
Stearic acid 6	30	3300	225	1125	2705	570
	35	3095	245	1250	2865	525
Pine tar 3	30	3100	225	1145	2735	550
	35	3290	225	1195	2840	525
Pine tar 6	30	3200	200	1155	2765	555
	35	3330	200	1205	2990	550

TS = tensile strength, lb. per sq. in.
M100 (300, 500) = modulus (lb. per sq. in.) at 100% (300%, 500%) elongation.
EB = elongation at break (%).

The abrasion tests were carried out in the manner already described (see Table 3)

Table 2 shows that the mixing containing 3 parts of stearic acid is a little stiffer than the others at the higher elongations, but otherwise the nature and proportion of the softener have very little influence on the stress-strain properties.

Marked differences, however, are again noticed in the abrasion losses. With both machines the pine tar mixings give higher losses, but whereas the difference on the Akron-Croydon machine is only some 10 per cent, it is very much larger on the du Pont machine. Increasing the proportion of softener always reduces the abrasion loss. It therefore appears that, both the nature and the quantity of the softener can affect the abrasion resistance, especially as measured on the du Pont machine, in a manner which would not be expected from the small effects of the softener on the stress-strain properties.

It will be noted that the influence of the softener on abrasion as measured by the du Pont machine is much the same in both the mercaptobenzothiazole and diphenylguanidine mixings (compare Tables 1 and 3). On the Akron-Croydon machine the effect of increasing the amount of softener is similar in both sets of mixings, although this is not true of the influence of the nature of the softener.

TABLE 3

Softener, and parts by weight per 100 parts of rubber	Akron machine, abrasion loss (cc.)	Du Pont machine		Energy used (H.P.)
		Abrasion loss		
		cc. per hr.	cc. per H.P.-hr.	
Stearic acid 3	0.189	4.7	235	0.0200
Stearic acid 6	0.169	4.3	220	0.0195
Pine tar 3	0.210	9.1	415	0.0219
Pine tar 6	0.193	7.5	355	0.0212

CONCLUSION

These experiments indicate that softeners can influence abrasion resistance, as measured by laboratory machines, in some manner other than by altering the stress-strain properties of the rubber. One possible explanation is that the softener acts as a lubricant to the abrasive surface. Since this surface, in

laboratory abrasion-testing machines, is relatively small, and comes repeatedly into contact with the rubber under test, it seems possible that it may become coated with a thin layer of softener that reduces its abrasive power. It would be interesting in this connection to try an abrasive machine in which a long continuous strip of abrasive material was used, no part of it being used more than once, so as to eliminate or minimize this lubricating effect.

The fact that the effect of the softener is more pronounced on the du Pont than on the Akron-Croydon machine lends support to the lubrication hypothesis, because on the former machine the rate of wear per unit area of abrasive is much greater. Thus in the present tests the volume of rubber abraded per hr. per sq. cm. of abrasive surface ranges from 0.03 to 0.11 cc. on the du Pont machine and from 0.0035 to 0.0045 cc. on the Akron-Croydon machine. On the other hand, if the softener acts as a lubricant, it would be expected to reduce considerably the friction between the abrasive and the rubber and hence the energy used in dragging the rubber over the abrasive surface. The energy figures given in the right-hand columns of Tables 1 and 3, however, show that there is relatively little variation between the different rubbers.

As a test of the lubrication hypothesis, it would be of interest to vary the conditions of test so that approximately the same amount of rubber per unit area of abrasive is abraded in a given time on both machines; this should show whether the phenomena observed under the present test conditions are due solely to the difference in rate of wear or to an inherent difference in the type of wear on the two machines. This could most conveniently be done by considerably reducing the load on the du Pont machine. In the original work on this machine[3] the load was standardized at 8 pounds, but no figures are quoted to show how abrasion loss varies with the load. As an addition to the present investigation, it is proposed to examine the effect of this variation with special reference to rubbers containing various amounts and types of softener.

Published data on the influence of softeners on the road wear of tire rubbers do not indicate anything like such large effects as are shown by the du Pont machine. This throws some doubt on the value of this machine for testing tire tread rubbers, a conclusion which is confirmed by information obtained from other workers.

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DETERMINATION OF RESISTANCE TO ABRASIVE WEAR. IX. INFLUENCE OF GRAIN IN TIRE TREAD RUBBER

J. R. SCOTT

INTRODUCTION

It has previously been shown[1] that in rubbers containing anisotropic fillers, *e.g.*, magnesium carbonate and clay, the resistance to abrasion, as measured by the Akron-Croydon machine, is very different according as the grain in the

disc-shaped test-piece lies in the plane of the disc, as in test-pieces prepared in the normal manner, or runs round the periphery. As abrasion tests are largely used for tire tread rubbers, it is important to know whether such grain effects are observed with rubbers of this type, because in a tire tread the grain runs round the periphery and, therefore, if abrasion resistance were found to depend on the direction of the grain, it would be necessary, to simulate service conditions, to prepare special abrasion test-pieces in which wear takes place along the direction of the grain. Such test-p eces may be prepared by cementing a strip of the rubber round the periphery of a wheel[2]. This method, however, is open to the objection that the tension set up in the outer surface of the strip by bending it into circular form may alter its abrasion resistance.

EXPERIMENTAL

Tests were accordingly made with a tire tread mix comprising rubber 100, sulfur 3.1, MPC black 38, zinc oxide 7.6, stearic acid 3.1, and mercaptobenzo-thiazole 0.76. Abrasion test-pieces were prepared in two ways: to give the grain (1) in the plane of the disc, (2) running round the periphery, by the methods previously described[1]. In type (1) the abrasion takes place on a surface corresponding to the edge of a calendered sheet (edge test), whilst in (2) it takes place on a surface corresponding to the flat face of the sheet (flat test). The (1) and (2) specimens were vulcanized simultaneously in a two-cavity mold for 30 minutes at 148° C. Two pairs of specimens were prepared. Abrasion tests on the Akron-Croydon machine were made at 58° F under the standard conditions.

Angle between planes of specimen and abrasive wheel	15°
Load on specimen	10 lb.
Speed of rotation of specimen	250 r.p.m.

The results were as follows:

	Abrasion loss, cc. per 1,000 revs. of abrasive wheel		
	Expt. 1	Expt. 2	Mean
(a) "Edge" test	0.268	0.272	0.270
(b) "Flat" test	0.264	0.272	0.268

SUMMARY

Results of the Akron-Croydon abrasion test on rubbers of the tire-tread type are not appreciably influenced by the direction of the grain. Consequently, it is considered satisfactory to test such rubbers by using the normal (edge) type of specimen, prepared by vulcanizing, in a suitable mold, a disc cut from a sheet of the unvulcanized stock about 13 mm. thick.

REFERENCES

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DETERMINATION OF RESISTANCE TO ABRASIVE WEAR. X. INVESTIGATION OF THE DURABILITY OF A BONDED ABRASIVE WHEEL ON THE DU PONT MACHINE

R. G. NEWTON AND J. R. SCOTT

INTRODUCTION

An investigation[1] has already been carried out to determine the uniformity existing among sheets of emery paper (No. 0, as supplied by the H. L. Scott Co.), normally used on the du Pont machine, and recommended by the American Society for Testing Materials. The results obtained in that investigation demonstrate that differences exist between the sheets of this paper of a nature which may vitiate a comparison between the abrasion resistances of two rubbers when the test is carried out by the ordinary procedure, and which therefore render the paper unsuitable as a standard abrasive surface when statistical methods have not been used in planning the experiment.

EXPERIMENTAL

The use of a solid bonded wheel was suggested by Morley and Scott[1], and the present investigation was undertaken to examine the durability of the 80 M (80 grit, grade M) Uniwheel abrasive wheel and to discover the extent to which its abrasive properties may vary with continued usage. This abrasive wheel is made by the Universal Grinding Wheel Co., Ltd., of fused alumina with a vitreous bond; the diameter is $6\frac{3}{4}$ inches and the thickness $\frac{3}{16}$ inch.

Only one wheel of this type was available for the experiment, so the results may be vitiated by the aging of the rubber samples, no control being available in the form of a wheel which was not subject to continued usage. On the other hand, in experiments on the Akron-Croydon machine[2] it has been shown that aging of the rubber was not noticeable over a period of 261 days. Again in the present investigation the tests on mixing A were spaced over 209 days, while those on mixing B were completed in only 28 days, significant decrease of abrasion loss being recorded in each case despite the different aging periods.

Two mixings, a tire tread and a solid mixing, were prepared for use in this investigation, the formulas being:

	M1319A	M1319B
Smoked sheet rubber	100	100
Sulfur	3.1	3.5
MPC black	38.2	—
Neosyl M.H.*	—	105
Zinc oxide	7.6	10
Mineral rubber	—	6
Stearic acid	3.1	2
Diphenylguanidine	—	0.85
Mercaptobenzothiazole	0.78	—
Benzothiazoyl disulfide	—	0.15

* Neosyl M.H. is a proprietary brand of silica containing a small amount of magnesium silicate.

The mixings were vulcanized in du Pont Abrasion molds for 30 minutes with a 5-minute rise to the required temperature, which was 148° C (50 lb.

steam pressure) for A and 134° C (30 lb. steam pressure) for B.   The vulcan-
izates were kept for about a week before starting the tests.   The specific
gravities were: A:1.119, and B:1.345.

The abrasion machine used conformed to the requirements of the A.S.T.M.
except that the arm was pivoted in the center so that the load on the samples
was equalized[1], the test conditions being as follows:

Total load pressing specimens against abrasive	8 lbs.
Speed of revolution of abrasive	37 r.p.m.
Mean linear speed of abrasive	48 ft. per min.
Air pressure used for blast to clean abrasive	25 lb. per sq. in.
Temperature of test	18–22° C

On the occasion of each test, three runs were made, each using a different
pair of specimens, this being the normal procedure with this machine.   Each
pair of specimens was given a preliminary run until the two specimens appeared
to be seating evenly; this run was not included in the test.   The actual test
run lasted 10 minutes, the samples being weighed before and after the test run.
Readings of the spring balance, attached to the arm holding the specimens,
were taken every two minutes during the test run; from these readings, using
the constants of the machine, the energy used in abrading the specimens was
determined, thus enabling the results to be expressed (1) as the volume loss in
cc. per hr., and (2) as the volume loss in cc. per horse-power hr.

RESULTS

The loss in weight of each specimen is given in Table 1, the terms L.H.S.
and R.H.S. denoting the left and right specimens as seen when facing the

TABLE 1
LOSS IN WEIGHT

Date of test	Interval of time (days)	Wear on wheel in interval (hrs.)	Specimen	Loss in weight (g.)			Average loss in weight	Percentage change in loss during 100 hrs.' wear
				Run 1	Run 2	Run 3		
			M.1319A					
12/5/38			R.H.S.	0.27	0.28	0.30	0.273	
	69	100	L.H.S.	0.26	0.25	0.28		10.2
20/7/38			R.H.S.	0.25	0.27	0.24	0.245	
	140	50	L.H.S.	0.24	0.25	0.22		7.4
7/12/38			R.H.S.	0.23	0.24	0.24	0.236	
			L.H.S.	0.25	0.23	0.24		
			M.1319B					
16/12/38			R.H.S.	0.50	0.47	0.53	0.512	
	14	50	L.H.S.	0.49	0.53	0.55		27.4
30/12/38			R.H.S.	0.45	0.42	0.42	0.442	
	14	50	L.H.S.	0.44	0.48	0.44		10.0
13/1/39			R.H.S.	0.41	0.44	0.40	0.420	
			L.H.S.	0.39	0.46	0.42		

The loss in weight is recorded to two significant figures only, since the errors of the test method do not
warrant greater accuracy.

machine. After the first test, the wheel was used for abrading various types of vulcanizates, until it had been subjected to a total of 50 hours' wear, when another test was made on the wheel. Another period of 50 hours' wear was given and a test again made. In the case of mixing A, the results of the test after the first 50 hours were discarded, since the individual results of the runs were exceptionally variable and one run gave a value of only half that of the other two; in this case, therefore, a further period of 50 hours' wear was given, making a total of 150 hours' wear on the wheel.

Table 2 records the volume losses in cc. per hr. and Table 3 the volume losses in cc. per H.P.-hr.

TABLE 2

VOLUME LOSS PER HOUR

Mixing	Date of test	Volume loss cc. per hour			Average volume loss per hr. (cc.)	Wear on wheel in interval (hrs.)
		Run 1	Run 2	Run 3		
M.1319A	12/5/38	2.9	2.9	3.0	2.9	100
	20/7/38	2.7	2.8	2.5	2.6	50
	7/12/38	2.6	2.5	2.6	2.5	
M.1319B	16/12/38	4.4	4.5	4.8	4.6	50
	30/12/38	3.9	4.0	3.9	3.9	50
	13/1/39	3.6	4.0	3.6	3.7	

TABLE 3

VOLUME LOSS IN H.P.-HOURS

Mixing	Date of test	Volume loss (cc. per H.P.-hr.)			Average volume loss (cc. per H.P.-hr.)	Wear on wheel in interval (hrs.)
		Run 1	Run 2	Run 3		
M.1319A	12/5/38	160	160	170	163	100
	20/7/38	150	160	140	150	50
	7/12/38	130	130	140	133	
M.1319B	16/12/38	300	300	320	307	50
	30/12/38	270	280	270	273	50
	13/1/39	250	280	250	260	

In this investigation, as was also found by Morley and Scott[1], there is no consistent difference between the values from the right and left hand sides of the machine, and consequently the differences between these pairs of values can be used to estimate the combined errors in the method of testing, between the various specimens, and between the sides of the machine. The coefficient of variation corresponding to these combined sources of variation (which may be called the minimum error) is 4.9 per cent for M.1319A and 5.0 per cent for M.1319B (on the basis of a single measurement—L.H.S. or R.H.S.—from a 10-minute test run). By making a suitable comparison of the means of the duplicates, it is possible to determine the variation among the results of the three runs on any one day, the coefficients of variation being 6.9 and 6.7 per cent for mixings A and B, respectively. Although these values are larger than the minimum error (about 5 per cent), the increase is not statistically significant, and there is, therefore, no reason to believe that any additional sources of error affect the variation between the runs made on one day. If, on the other hand, a comparison is made between the tests before and after a period of wear on the abrasive wheel, the coefficients of variation are (on the same basis) 18.0

and 25.4 per cent, for A and B, respectively, which values are very significantly greater than the minimum error inherent in the method, and the conclusion must be drawn that very real differences occurred between the three lots of tests, especially since the change is continuous and in the same direction for both A and B.

In the absence of control tests on a different wheel, there is no positive proof that this very definite change is due solely to the wearing or clogging of the wheel, but, in view of the previous evidence as to the absence of an aging effect, it is very probable that the difference is due to the treatment during the intermediate periods of testing.

The coefficients of variation of the H.P. method of expressing the results are given in Table 4. It will be seen that a very large difference between the tests can be demonstrated in this case also. Figures are not given for the variation in volume loss, since they are directly proportional to the weight loss. The figures for the variation in weight loss are collected in Table 4.

It can be readily seen from Tables 1, 2 and 3, that the loss of abrasive power of the wheel per hour of wear during the interval is not the same for the two

TABLE 4

COEFFICIENTS OF VARIATION (ON THE BASIS OF ONE MEASUREMENT—
L.H.S. OR R.H.S.—FROM A TEN-MINUTE TEST RUN)

	Type of results			
	Weight loss per hr.		Volume loss (cc. per H.P.-hr.)	
Type of variation	A	B	A	B
Minimum variation, representing the errors in the method, the variation between the specimens, and between the sides of the machine	4.9	5.0	—	—
Variation between runs carried out on the same day	6.9	6.7	4.5	4.4
Variation between tests carried out before and after subjecting the abrasive wheel to wear	18.0	25.4	18.8	15.4

intervals, but this is not surprising, since a large number of very different vulcanizates were tested on the wheel during these intervals, and the wear or clogging may have been more severe during one interval than the other.

In all cases the wearing of the wheel produces a very definite effect.

It is interesting to note that the results obtained on one day show less variability when they are calculated on the H.P. basis, but an insufficient number of results is available for definite conclusions to be drawn.

Since the coefficient of variation is the standard deviation expressed as a percentage of the mean value, twice the coefficient of variation gives a measure of the uncertainty to be attached to the value of a result from one measurement (i.e., R.H.S., or L.H.S.) e.g., about ±14 per cent for the weight or volume loss and about ±9 per cent for the volume loss per H.P.-hr. In expressing these results, therefore, there is no justification for employing more than two significant figures. The test result is normally based on six such measurements, so that the percentage uncertainty on a test result will be about ±5 and ±3.5 per cent, respectively.

In this connection it is interesting to compare the results with those given by Morley and Scott.[1]

Coefficient of variation due to method of testing and to the specimens, *i.e.*, the minimum error	5.1%	all on the basis of one measurement—L.H.S.
Coefficient of variation between tests on any one paper	9.3%	or R.H.S. from a 10-
Coefficient of variation between the emery papers	18.0%	minute run.

The variation due to the method of testing, thus appears to be almost exactly 5.0 per cent whether the papers or the abrasive wheel are used, and it appears to be independent of the ease with which the samples are abraded, since M.1319B abrades about twice as quickly as M.1319A.

SUMMARY

The results reported here entirely confirm those of Lambourn[3], who found that marked deterioration occurred with all the types of abrasive wheel which he used. In the present investigation on a bonded wheel, it was concluded that the wheel was appreciably less abrasive after each period of 50 hours' wear, while Lambourn concluded that one side of a wheel can be used for a period of two months when subjected to 40 hours of wear per week.

Lambourn also concluded that the deterioration is caused by smoothing or disintegration of the abrasive particles and not by clogging with rubber dust, and points out that variation in abrasive wear can be compensated by daily tests on samples of a standard compound. He also states that a grain coarser than 24 should not be used, since the abrasion is too rapid.

Since the standard emery papers vary among themselves, and the bonded abrasive wheel deteriorates when it is used, it is evident that attention should be paid to the statistical planning of these tests, so that these factors can be reduced or eliminated.

The coefficient of variation of a test result, *i.e.*, the mean of three 10-minute runs, each on duplicate specimens, (six individual readings) as normally measured, seems to be independent of the type of abrasive employed (emery papers or bonded disc) and the uncertainty of the result is about ±5 per cent when measured on the basis of volume loss per hour and about ±3.5 per cent when determined as the volume loss/H.P.-hr. Test results will therefore be required to differ by about 7 and about 5 per cent, respectively, for a significant difference to be demonstrated.

REFERENCES

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DETERMINATION OF RESISTANCE TO ABRASIVE WEAR. XI. INFLUENCE OF THE TYPE OF ABRASIVE

R. G. NEWTON, J. R. SCOTT, AND W. H. WILLOTT

INTRODUCTION

Abrasion-testing machines do not all use the same type of abrasive, and even among abrasive papers or bonded wheels of the same make and grade, considerable variation may exist, so much so, indeed, that it is doubtful whether

a strictly reproducible standard abrasive can be obtained. This would not be serious if all rubbers responded in the same way to variations in the abrasive, because by expressing the test result as a ratio to that for a standard rubber, a figure (abrasive index) independent of the type of abrasive would be obtained.

The use of a standard comparison rubber was in fact proposed many years ago in a tentative specification for pneumatic tire covers[1], and both the American Society for Testing Materials[2] and the Deutscher Verband für die Materialprüfungen der Technik[3] have adopted the principle of the abrasive index. The subject of abrasive indices acquired added importance during the war as a result of the proposal that the durability of war-time sole and heel compounds should be assessed and controlled by measurements of an abrasive index.

It is clearly important to know whether and to what extent the abrasive index of a given rubber depends on the type of abrasive used. Some information on this point is deducible from published data obtained on the New Jersey Zinc Co.'s abrasion machine[4] and on a machine[5] apparently similar to that now standardized by the Deutscher Verband für die Materialprüfungen der Technik[3]; these data will be referred to later. However, neither of these machines is used widely, if at all, in this country, and it is therefore believed, that the results described in this report, relating to the well known du Pont (Grasselli) machine, will be of interest to the many users of this machine.

TABLE 1

COMPOSITION OF RUBBERS

Mix No.	1	2	3	4	5	6	7
Rubber	100	100	100	100	75	100	100
Whole-tire reclaim	—	—	—	—	45	—	—
Sulfur	3.1	3.5	3.0	2.0	3.75	2.75	2.5
Blanc fixe	—	—	—	20	—	—	—
MPC black	38	—	100	—	—	—	—
FT black	—	—	—	—	80	—	—
China clay	—	—	—	—	—	50	—
Lithopone	—	—	—	30	—	—	—
Magnesium carbonate	—	—	—	43	—	—	—
Silica (Neosyl-MH)	—	105	—	—	—	—	—
Whiting	—	—	—	—	—	—	200
Zinc oxide	7.6	10	10	200	19	5	5
Mineral oil	—	—	—	2	—	—	—
Mineral rubber	—	6	5	—	—	—	—
Stearic acid	3.1	2.0	2.0	2.0	1.9	1.0	2.0
Coumarone resin	—	—	—	—	6	—	—
Butyraldehydeaniline	—	—	—	—	0.75	—	—
Diphenylguanidine	—	0.85	1.0	—	—	—	—
Mercaptobenzothiazole	0.76	—	—	—	—	—	0.75
Dibenzothiazoyl disulfide	—	0.15	—	—	—	0.75	—
Tetraethylthiuram disulfide	—	—	—	0.5	—	—	—
Vulcanization, temperature (° C)	148	135	141	141	141	141	141
minutes	30	30	45	13	20	40	30

EXPERIMENTAL

Tests were made on a du Pont machine of standard type except for the following modifications: (1) the arm carrying the specimens is pivotted at the point of attachment to the rod by which the load is applied, with the idea of equalizing the pressure on the two specimens (this improvement was suggested as a result of a previous investigation[6]); (2) the arm is fitted with a dashpot to prevent the rapid oscillations that are otherwise likely to occur.

Standard molded specimens of various rubbers (see Table 1 for composition) were used.

The abrasives examined comprised ten types of abrasive paper and seven types of bonded abrasive wheel, these being of the same internal and external diameters as the standard paper discs and $\frac{3}{16}$ inch thick, so as to fit on the machine in place of the usual paper. As the tests were made at intervals over a fairly long period, the experiments with the standard (emery No. 0) paper were repeated towards the end of the series.

RESULTS

Mean results of six tests (three 10-minute runs each on a new pair of specimens) are given in Table 2, relating to two rubbers on all the abrasives, and Table 3, relating to all the rubbers on three abrasives. Results are denoted by

TABLE 2

Maker (a)	Abrasive Description	Abrasion loss				Abrasive index of Mix 2	
		Mix 1		Mix 2			
		D./hr.	D/HP	D./hr.	D/HP	D./hr.	D/HP
	Papers						
(b)	Emery No. 0	3.10	162	6.64	441	47	37
(b)	Emery No. 0	3.19	161	5.39	352	59	46
D	Garnet 2/0. 100 ECL.	4.39	247	12.2	728	36	34
D	Garnet 3/0.	3.92	199	7.84	494	50	40
D	Garnet 4/0.	4.52	234	9.08	534	50	44
D	Garnet 5/0. 180 ECL.	2.52	103	6.96	417	36	25
D	Garnet 5/0. 180 ECL.	3.04	147	5.70	357	53	41
D	Garnet 5/0. 180 ECL.	3.10	151	4.63	280	67	54
D	Durexalo 3/0	6.68	373	11.9	751	56	50
D	Durexalo 4/0	4.23	245	8.84	475	48	52
D	Durexalo 5/0. 180 ECL.	3.28	167	7.07	426	46	39
D	Durexalo 5/0. 180 ECL.	3.84	194	8.11	495	47	39
(c)	(c)	1.94	121	2.41	183	80	66
(c)	(c)	1.77	101	2.61	190	68	53
(d)	(d)	2.39	97	6.88	430	35	23
	Wheels						
N	Alundum 80–M8	4.99	246	11.7	756	43	33
N	Crystalan 3780–M8	2.91	114	4.27	269	68	42
C	E60	3.45	192	2.75	180	125	107
C	E60	3.10	175	3.31	221	94	79
C	E60	3.22	186	2.75	190	117	98
U	80M	7.08	462	6.86	456	103	101
U	100L	2.80	130	3.95	270	71	48
U	100M	3.05	155	3.25	235	94	66
U	Bauxilite Grade L	1.83	84	1.63	117	112	72

Notes.—(a) D = Durex Abrasives, Ltd.; N = Norton Grinding Wheel Co., Ltd.; C = Carborundum Co., Ltd.; U = Universal Grinding Wheel Co., Ltd.
(b) Standard paper as supplied by the Henry L. Scott Co. for the du Pont machine.
(c) Not known; both these papers were of the same kind.
(d) Not known; both these papers were of the same kind.

D/hr. (abrasion loss in cc. per hour) and D/HP (cc. per horse-power-hour). The abrasive index is the ratio of the abrasive resistance to that of the standard rubber, taken as 100 (the higher the abrasion loss the lower the index). In Table 2 the tire-tread rubber, Mix 1, is taken as the standard; in studying the results in Table 3, Mix 2 had to be used as standard, because the data for Mix 1 were incomplete.

TABLE 3

Maker	Abrasive* Description		1	2	3	4	5	6	7
					Abrasion loss for Mix No.				
—	Emery No. 0 paper	D/hr.	—	5.84	2.33	8.30	6.66	7.08	6.81
		D/HP	—	380	146	540	432	462	490
C	E60, wheel	D/hr.	3.26	2.94	0.83	6.38	3.53	8.88	4.92
		D/HP	184	197	52	388	216	525	306
U	80M, wheel	D/hr.	7.08	6.86	3.35	13.6	9.71	11.6	10.8
		D/HP	462	456	210	866	622	728	777

* See Table 2.

DISCUSSION

SERIES I (TABLE 2)

The right-hand two columns of Table 2 show that the abrasive index varies considerably according to the type of abrasive used, the range of variation being from 35 to 125 for D/hr., and from 23 to 107 for D/HP.   Estimates of the durability of Mix 2 made with different abrasives thus vary by as much as 4 to 1, and indeed by suitably choosing the abrasive, this rubber can be made to appear either better or worse than the standard.

The discussion of these results is rendered difficult because an analysis of variance of even the more consistent D/hr. results from Table 2 shows that several effects are highly significant.   The analysis was carried out on ten papers and the two wheels, from Maker N, which agreed most closely with the papers; the analysis is given in Table 4, in terms of a single 10-minute run on one specimen, *i.e.*, one side of the machine.

In the first place, there is now a significant difference in the wear produced by the left- and right-hand sides of the machine, the former causing the greater wear in practically every case.   This is in contrast to the results found by Morley and Scott[6] and by Newton and Scott[7], and would seem to indicate wear in the support.   Machines in other laboratories have been found to develop the same defect, and it would appear that special care must be taken to plan the experiment with a view to eliminating its effect, by reversing the positions of the test-pieces from one side to the other, taking care to see that they are properly reseated, if necessary by giving them a further running-in. There are also significant, but relatively much smaller, differences between the three runs on the abrasives, showing that they become less abrasive with continued wear.   This aspect complicates the comparison of samples by reversing

TABLE 4

ANALYSIS OF VARIANCE

Source of variation	Sum of squares	d.f.	Variance
Between mixings	122.2315	1	122
Between abrasives	104.4061	11	9.5
Between sides	4.9470	1	4.9
Interation M × A	19.9800	11	1.8
Between runs	1.5440	2	0.77
Pooled interaction with runs, *i.e.*, R × M, R × A, R × M × A	7.3991	46	0.16
Pooled interactions with sides (regarded as error)	3.2920	71	0.046
Total	263.7997	143	

their positions from left to right, as suggested above, but the procedure to be taken is discussed briefly in the general conclusions to this paper. The variation between the mixings, and between the abrasives, are both naturally very large (see Table 4), but it is interesting to note that the interaction between mixings and abrasives is the fourth largest item, despite the fact that this analysis covers only the most uniform papers and wheels. This item corresponds to the variation in abrasive indices noted above but, beyond noting the magnitude of the variance derived from it, no detailed discussion of the effect will be offered in the present report because a much fuller study of it is being made both on the du Pont and on the Akron-Croydon machine. The following discussion of abrasive indices is, therefore, on a simple basis, and the logarithm of the abrasive index is generally used in preference to the index itself. (In expressing a result as an index or ratio to a standard, it seems preferable for various reasons to use the logarithm of the ratio). The extent of the variation among a set of abrasive index figures is then conveniently expressed as the standard deviation of these logarithmic values.

Table 5 summarizes the variation among the abrasive indices in Table 2.

TABLE 5

LOGARITHM (TO BASE 10) OF ABRASIVE INDEX OF MIX 2

	D/hr.	D/HP
Average for all abrasives	1.72	1.63
Average for papers only	1.70	1.62
Average for wheels only	1.75	1.64
Standard deviation: all abrasives	0.17	.18
Standard deviation: papers only	0.10	0.12
Standard deviation: wheels only	0.18	0.20

The following conclusions can be deduced from Tables 2 and 5.

(1) D/HP gives a lower average value for the index than D/hr., the corresponding actual indices being 43 and 52, respectively. Table 2 shows, moreover, that individual D/HP indices are lower than the corresponding D/hr. indices in every case but one. A definite explanation as to why the D/HP indices are usually lower than the D/hr. indices is not possible at present. An important fact, however, is that the difference can exist, so that it is not immaterial which method is adopted for calculating abrasive indices from the du Pont test. More attention is, however, given to the D/hr. values in this discussion.

(2) The observed variation between indices from different abrasives, as shown by the standard deviation figures in Table 5, is much greater than could arise from experimental errors (this source of variation is represented by a standard deviation of about 0.02 or 0.03 on the log index).

(3) Abrasives that produce rapid wear do not tend to give either higher or lower indices than the slower-acting abrasives. The index thus apparently does not depend on the degree of abrasiveness.

(4) The variation of the index is nearly the same, whether D/hr. or D/HP is used, as is shown by the substantial equality of the two standard deviation figures. This means that neither method of calculating the test result has any advantage over the other as regards reducing the dependence of the index on the type of abrasive.

(5) The average D/hr. index for papers (1.70) is lower than that for wheels (1.75), and this difference is one cause of the big variation among the abrasives as a whole.   When papers alone are considered, the variability is only half as great (standard deviation 0.10 as compared with 0.18).   From the point of view of variability in abrasive index, it would thus appear preferable to use only abrasive papers on the du Pont machine, but other considerations, such as greater permanence of bonded wheels, might well outweigh this advantage, see Section IV.4.

SERIES II (TABLE 3)

The abrasive indices relative to Mix 2 as standard ($=100$), and arranged approximately in decreasing order, are shown in Table 6.

TABLE 6
ABRASIVE INDEX

Mix No.	Emery No. 0 paper		E60 wheel		80M wheel	
	D/hr.	D/HP	D/hr.	D/HP	D/hr.	D/HP
3	250	265	355	380	205	220
2	100	100	100	100	100	100
1	—	—	89	107	98	100
5	87	87	83	91	91	74
7	85	78	60	65	63	59
6	83	81	33	37	59	63
4	71	71	46	51	50	53

Again the indices vary according to the abrasive used, but only in a few cases is the order of merit of two rubbers changed by changing the abrasive. A more detailed study of these results leads to the following conclusions.

(1) The D/hr. and D/HP indices are usually close together, and there is no tendency, such as was noted above, for the D/HP indices to be lower.

(2) The variations among the indices for the same rubber on different abrasives are about the same as were found in Series I, being, in fact, slightly greater than the variation among papers in that series (standard deviation of log index 0.115 and 0.10 for D/hr. and D/HP, respectively).   Again the D/hr. and D/HP indices are about equally variable.

NONUNIFORMITY OF ABRASIVE PAPER

The above results show that large discrepancies between measurements of abrasive indices in different laboratories or on different machines may arise if no selection is exercised in regard to the abrasive paper used, because the observed standard deviation of about 0.10 on the log index means that as often as not two measurements made on different kinds of paper would differ by at least 25 per cent.

Standardization of the abrasive paper is thus obviously desirable.   It is important to know, however, to what extent a given kind of paper varies in its abrasive characteristics.   Previous work[8] has shown that nominally identical paper discs (as used on the du Pont machine), or different portions of a single large sheet of paper, vary markedly in abrasive action, and it is possible to estimate how this affects the abrasive index from the data of Schlobach and Bussen[5], who tested 22 identical rubber specimens side by side on a rotating abrasive-paper-covered drum, so that each specimen was abraded by a different

part (track) of the paper. Data are given for two rubbers, so the abrasive index of one relative to the other can be calculated for each of the 22 "tracks" on the paper; the standard deviation of the log index is found to be about 0.04 (0.03 and 0.05 in duplicate experiments using different sheets). This variation, between different parts of a 40 × 40 cm. sheet of paper, is actually greater than that found by the same workers for the variation between indices obtained on different types of paper (namely, 0.022).

Another estimate of the effect of nonuniformity of the paper can be obtained from the results in Table 2 for the two discs of emery No. 0 paper, three of Garnet 5/0.180 ECL, two of Durexalo 5/0.180 ECL, and two of an unknown grade of paper, together with a duplicate set of figures (not shown) for the Garnet and Durexalo papers, using different batches of the two rubbers. These data indicate about the same variability between the indices obtained on nominally identical papers as between those obtained on different papers (standard deviation of log index 0.08 and 0.10 for D/hr. and D/HP, respectively (see the value of 0.09 for different papers in Table 5). No great accuracy can be claimed for these figures, because the number of tests was small. It does appear, however, that even when nominally identical papers are used the abrasive indices for the same rubber may vary considerably, possibly as much as when using different types of paper.

GENERAL CONCLUSIONS

The main conclusion from these experiments is that close agreement cannot be expected between abrasive indices obtained on different kinds of abrasive, and that a variation represented by a standard deviation of about 0.10 on the log index must be regarded as normal. It is interesting to compare this figure with corresponding ones deduced from published data[9].

Type of machine	New Jersey Zinc Co.	Schlobach and Bussen (b)
No. of abrasives examined	2 or 3 (a)	5
No. of rubbers examined	8	11
Standard deviation of log index	0.14	0.022

Notes: (a) In different experiments.
(b) See Schlobach and Bussen[5]. This is apparently the machine since standardized by the Deutscher Verband für die Materialprüfungen der Technik[3].

The variability on the New Jersey Zinc Co. machine, which uses a bonded abrasive track, is about the same as found in the present investigation for bonded abrasive wheels, namely, 0.18–0.20 (see Table 5). The smallness of the variability observed by Schlobach and Bussen is doubtless due in part to the fact that in these tests every specimen was abraded over a very large area (1,600 sq. cm.) of paper; this minimizes the effect of nonuniformity of the paper, which otherwise would contribute to the observed variation between types of abrasive. Using their data for the nonuniformity of the paper, it is estimated that in tests using a small area of paper, as in the du Pont test, the figure of 0.022 would be increased to about 0.04 or 0.05.

To illustrate more clearly what the effect of different abrasives on the abrasive index means in practice, the following example may be cited. If the same rubbers were to be tested against the same standard in laboratories that used different papers not specially selected for similarity, then it might well be found, on comparing the different laboratories' indices for the same rubber,

that one laboratory's index was twice as great as another's, and that frequently one index would be at least 50 per cent greater than the other.

This example relates to variation of the abrasive index caused by using different types of abrasive paper. The available evidence seems to show, however, that discrepancies perhaps equally large may arise from the non-uniformity of a given type of paper. It thus seems that a method in which one and the same large area of paper is used for testing the different rubbers to be compared, as was done by Schlobach and Bussen[5], would give more uniform results than the usual du Pont technique, using a different piece of paper for each rubber. The advantage of testing different rubbers on the same piece or pieces of paper has already been pointed out in an earlier report in this series[6].

It would seem that the ideal method for the du Pont machine would be to abrade one specimen of the rubber under test and one of the standard simultaneously, one on each side of the arm. This can be done if the arm is pivotted, thus permitting different rates of wear on the two specimens. Okita[10] has done an experiment of this nature, but without the pivot, and claims that reliable results are not obtainable; his results, however, are not entirely free from suspicion because some of his samples increased in weight. On the other hand, experiments with the pivotted arm have proved successful if they are

TABLE 7

ABRASIVE INDICES FROM SPECIAL EXPERIMENTS

Abrasive used	Test procedure	Abrasive indices		Discriminating Power
		EPC	HMF	
Paper	Normal	91	108	11.5
	Special	94	108	15.5
Wheel	Normal	84	134	68
	Special	85	136	75

combined with a statistical design of the experiment. Two different rubbers are tested together, one on each side of the machine, and they are then reversed (right and left) and tested again. This allows the differences between the rubbers, between the sides, and between the runs to be obtained independently of one another. Suitable replication of the experiment also permits the error of test to be measured, and the same concept can be extended to more than two rubbers. The results of such an experiment, made on rubbers containing MPC, EPC, and HMF blacks, are given in Table 7 in the form of abrasive indices, the MPC compound being taken as 100.

The normal experiments used pairs of samples of the same kind, tested together in the usual manner, while the special tests compared different rubbers on each side. (The full details of the test, and an account of the general theory of this kind of experiment, will be given later, in another report.)

It is clear that there are no significant differences in abrasive index between the normal and special tests, and that the wheel produces greater separation between the rubbers. This greater separation does not necessarily involve greater discrimination because the errors of test may be different, but the discriminating power can be obtained by dividing the variance between the rubbers by the error variance, and the results are inserted in Table 7. It can be seen that the wheel gives much more discrimination than does the paper, and

also that the special test technique has, in each case, superior power of discrimination.

SUMMARY

Tests with the du Pont machine show that the practice of expressing abrasion test results as an abrasive index, *i.e.*, abrasion-resistance relative to a standard rubber, does not enable different types of abrasive to be used indiscriminately because these are found to give widely different abrasive indices for the same rubber; thus, some abrasives may give four times as high an index as others.   If attention is confined to abrasive papers, as distinct from bonded abrasive wheels, this variation is reduced, but is still large enough to be a serious factor in accurate work.   It is clear that, even when this comparative method of testing is used, standardization of the abrasive paper is essential to reduce discrepancies between results obtained in different laboratories.

Discrepancies will still exist, however, because abrasive paper is not uniform, and there is evidence that abrasive indices determined on different portions of the same paper may differ as much as those from different types of paper.   To minimize the effect of this nonuniformity, two courses are open. (1) All the rubbers to be compared could be abraded on one and the same area of paper, preferably a large area to avoid wearing the surface, *e.g.*, by giving each rubber a short run on each of the several paper discs used, instead of using a different disc for each rubber.   (2) Different specimens could be tested on the two sides of the machine provided this has a pivotted arm.   It is shown that this technique has several advantages.

The factors that cause the abrasive index to vary from one abrasive to another are not known; it appears, however, that the degree of abrasiveness is not a determining factor.

The two methods of calculating abrasion loss—as cc. per hr. and cc. per H.P.-hr.,—usually do not give the same abrasive index; in any standard test method it is therefore essential to state which is to be used.   The variation of the abrasive index from one abrasive to another is the same whichever method of calculation is used.

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DETERMINATION OF RESISTANCE TO ABRASIVE WEAR. XII. COMPARISON OF AKRON AND DU PONT ABRASION MACHINES. VALUE OF AN ABRASIVE INDEX

J. R. SCOTT

INTRODUCTION

Reference has already been made[1] to the proposal that the durability of rubbers should be assessed and controlled by measurements of their abrasive index, *i.e.*, abrasion resistance relative to that of a standard rubber. In considering such a scheme, the question immediately arises, whether different abrasion machines give the same abrasive index for the same rubber and, if not, whether any simple conversion factor or formula enables the indices obtained on the different machines to be converted one to the other. From the fact that different types of abrasion machine normally use different abrasives, it may be predicted, on the basis of previous work[1], that the answer to both of these questions is in the negative. It is, nevertheless, valuable to have a direct answer based on tests with different machines, and this is possible from data obtained on a large number of sole and heel stocks. These were tested on behalf of the Sole & Heel Panel of the Federation of British Rubber & Allied Manufacturers' Associations, to whom we are indebted for permission to use the results as the basis of this report.

Reference is made also in this report to previous comparisons between various abrasion machines, recorded in the literature, which indicate broadly the same conclusions as the present experiments.

EXPERIMENTAL

Seven firms submitted samples (31 in all) of unvulcanized sole and heel stocks, which were vulcanized in the R.A.B.R.M. Laboratories, under the conditions indicated by the firms, to give Akron and du Pont abrasion specimens.

For the purpose of selecting a suitable reference standard, two types of mix were examined, namely, a typical wartime heel mix and mix B proposed by the American Society for Testing Materials (for use as an abrasion standard).

Standard heel mix		A.S.T.M. B mix	
Whole-tire reclaim (alkali)	70.0	Rubber	100.0
Sulfur	1.0	Sulfur	3.5
MPC black	10.0	MPC black	30.0
SRF black	5.82	Zinc oxide	20.0
Zinc oxide	2.0	Stearic acid	2.0
Mineral rubber	8.0	Di-ortho-tolylguanidine	1.25
Plasticizer	0.25	Phenyl-beta-naphthylamine	1.0
Stearic acid	1.0		
Pine tar	1.63		
Accelerator (Vulcafor-F)	0.31		

Samples of each of these mixes were made by two of the manufacturers and vulcanized in the R.A.B.R.M. Laboratories under the following conditions.

Standard heel mix, manufacturer II: 25 min.* at 141° C
Standard heel mix, manufacturer VI: 30 min.* at 141° C
A.S.T.M. B mix, manufacturer   II: 65 min.   at 141° C
A.S.T.M. B mix, manufacturer   VI: 65 min.   at 141° C

* Optimum determined from tensile properties.

Test conditions were as follows: *Akron machine*: Method described by Dawson and Porritt[2], using a 36H abrasive wheel (Universal Grinding Wheel Co.); *du Pont machine:* Method A of the A.S.T.M.[3], but with the machine modified as previously described[1], and using Garnet Paper 5/0. 180 ECL (Durex Abrasives, Ltd.).

RESULTS

The results of the abrasion tests are given in Table 1, under the heading "Abrasion loss"; this is expressed as cc. per 1,000 revolutions of the abrasive wheel in the case of the Akron machine, and as cc. per hour or per H.P.-hour with the du Pont machine.

It may first be noted that there is a big difference between the two batches (Nos. 362 and 393) of the standard heel mix, doubtless because different lots of whole-tire reclaim were used by the two manufacturers. For this reason the

TABLE 1

Manu-facturer	Stock reference no.	Type	Abrasion loss			Abrasive index		
			Akron	Du Pont (cc. per hr.)	Du Pont (cc. per HP-hr.)	Akron =Ak	Du Pont (cc. per hr.) =D/hr.)	Du Pont (cc. per HP-hr.) =D/HP)
II	362	standard heel	0.63	17.5	1085	—	—	—
VI	393	standard heel	0.995	15.9	1000	—	—	—
II	419	ASTM B	0.335	7.3	380⎫	100	100	100
VI	420	ASTM B	0.395	6.9	395⎭			
I	3131	heel	1.79	8.7	625	20.5	81.5	62
	3132	heel	1.58	9.6	660	23	74	59
	3133	sole	2.38	10.1	755	15.5	70.5	51
	3134	sole	2.27	10.0	820	16	71.5	47
II	3143	sole	1.69	12.5	900	21.5	57	43
	3144	heel	2.84	11.6	870	13	61.5	45
	3145	heel	1.40	9.6	645	26	74	60
	3146	sole	1.87	10.8	755	19.5	66	51
	3147	heel	1.97	12.1	850	18.5	58.5	46
III	3148	heel	1.04	8.1	625	35	87.5	62
	3149	heel	1.00	7.6	500	37	93.5	77.5
	3150	sole	1.01	7.5	485	36	94.5	80
	3151	sole	1.39	11.4	790	26.5	62.5	49
	3152	sole	1.42	9.6	695	26	74	56
IV	3071	heel	1.08	9.7	670	34	73	58
	3072	heel	0.76	7.6	480	48	93.5	80.5
	3073	sole	1.10	8.8	640	33.5	81	61
	3074	sole	1.36	9.7	675	27	73	57.5
	3075	heel	1.89	11.1	810	19.5	64	48
V	3185	heel	1.59	13.6	910	23	52.5	42.5
	3186	sole	2.44	16.7	1170	15	42.5	33
	3187	heel	1.81	17.2	1155	20.5	41	33.5
	3188	sole	1.11	10.2	660	33	70	59
	3189	sole	1.07	9.9	665	34.5	72	58
VI	3255	heel	1.50	10.3	725	24	69	53
	3256	heel	1.19	12.8	760	30.5	65.5	51
	3257	sole	2.47	18.4	1455	15	38.5	26.5
	3258	sole	1.06	10.4	655	34.5	68	59.5
	3259	sole	2.65	16.5	1170	14	43	33
VII	3304	—	1.11	11.2	725	33	63.5	53
	3305	—	1.65	12.5	940	22	56.5	41

A.S.T.M. B mix was adopted as the standard of reference, taking the means of the figures for the two batches (Nos. 419 and 420). The abrasive index in Table 1 is the abrasion resistance relative to this standard as 100, so the bigger the abrasion loss the smaller the index. The abbreviations "Ak," "D/hr.," and "D/HP" are used to denote the abrasive indices according to the Akron, du Pont (loss per hour), and du Pont (loss per H.P.-hour) tests, respectively.

DISCUSSION

COMPARISON OF AKRON AND DU PONT RESULTS

In every case the Akron machine gives a lower index (ranging from 13 to 48) than the du Pont machine, and with the latter the D/HP index is always lower (26.5 to 80) than the D/hr. index (38.5 to 94.5). The geometric average of the indices for the 31 sole and heel rubbers are: Ak.: 24; D/hr.: 66; D/HP: 51. Published data do not indicate such large differences between the average indices given by different methods; indeed only in one case[4] can a real difference be claimed; in the other cases[5] the differences are negligible. It must be noted, however, that the difference between the average indices given by the two methods depends on which rubber is chosen as standard in calculating the indices, so it can never be stated with certainty that two abrasion methods will always give the same average indices.

The fact that different methods do not give the same index would not be serious if the indices by the various methods were closely related; this point is fully discussed below.

Another important point to be decided is which test shows the biggest differences between different rubbers, and so discriminates most clearly between them. In considering these problems it is often convenient to use the logarithm (to the base 10) of the index; when expressing a result as an index, or ratio to a standard, indeed, it is more correct to use the logarithm rather than the ratio itself.

Discrimination between rubbers

It is interesting to note that the dispersion of the A values is greater than either set of du Pont values, but this does not necessarily mean that the discrimination is better because the errors of the Akron test are greater than in the du Pont test. The best measure of the discriminating power of a test is given by the ratio of the variance between the rubbers to the error variance, from which it appears that the D/hr. values show the greatest discrimination. If the calculations are made on the logarithms of the abrasive indices, and the dispersion is measured by the standard deviation of these values, the following values are obtained:

	Ak.	D/hr.	D/HP
Dispersion	0.15	0.10	0.11
Relative discriminating power	13.4	15.6	7.2

In published comparisons of abrasion test methods[6] there is, with one exception, no definite indication that any one method is more discriminating than another, but the small number of rubbers tested (10 or less) renders the evidence inconclusive. The exception[4] shows the Goodrich machine, and possibly the New Jersey Zinc Co. and sand-blast machines, to have greater dispersion than the Akron machine.

Use of datum line

In using the abrasive index to judge the suitability or otherwise of sole or heel rubbers, a minimum permissible index or datum line would presumably be fixed. To show how this would operate, according to the present results, the 31 sole and heel rubbers have been divided by an arbitrary datum line into a good group of 16 rubbers and a bad group of 15 rubbers.

When this is done with each of the three sets of indices in Table 1 it is found that in 8 cases a good rubber according to the Ak. index is poor according to the D/hr. index, or *vice versa;* in 4 cases a good rubber by the Ak. index is poor according to D/HP, or *vice versa.* On the average, therefore, Akron and du Pont tests give contradictory verdicts for about 6 out of the 31 rubbers,
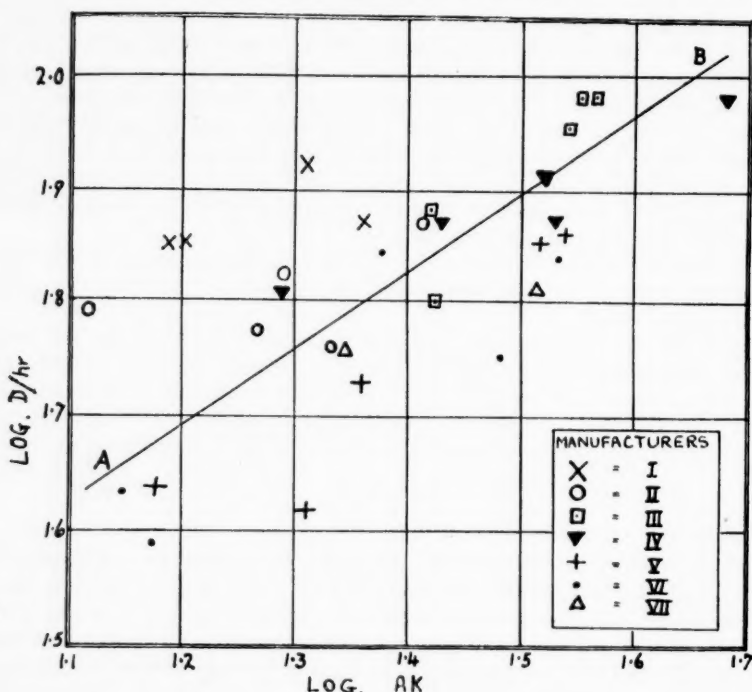

FIG. 1

or once in 5 times. There is about this same chance of obtaining contradictory verdicts if the datum line is so placed that the good group contains 25 and the bad group 6 rubbers.

Quantitative relation between Akron and du Pont indices

Figure 1 shows log D/hr. (*i.e.*, the logarithm of the index by the du Pont test, taking abrasion loss per hour) plotted against log Ak. for the 31 rubbers; if log D/HP is taken instead of log D/hr. a diagram of very much the same general appearance is obtained.

It is obvious that the points, though scattered, tend to lie along a straight line AB, and it is easily shown that the equation for this line is:

$$\log D/hr. = 0.68 \log Ak. + 0.87 \qquad (1)$$

The corresponding equation for the D/HP data is:

$$\log D/HP = 0.75 \log Ak. + 0.66 \tag{2}$$

These equations enable indices obtained on the one type of machine to be converted (approximately) to those for the other; hence a datum line fixed from tests on the one could be used to calculate the datum line appropriate to the other.

If the points in the figure and the corresponding D/HP graph lay exactly on the lines represented by the equations, these conversions and calculations could be made exactly, but as they do not, it follows that the equations are only approximations and that calculations based on them are subject to error. It thus becomes important to know how big this error is likely to be.   These errors are obtained from a regression-analysis of points in relation to the straight line, but they can easily be demonstrated by considering the difference between an index measured directly on the Akron or du Pont machine and that calculated by Equation (1) or (2) from the index measured on the other machine. This difference, which is the error arising in the interconversion of indices, may be considerable, as the following summary of the data for the 31 rubbers shows (Table 2); this Table gives also the root mean square of the differences between calculated and measured logarithmic indices, which is the most exact method of expressing the magnitude of the errors.

TABLE 2

ERROR EXPRESSED AS DIFFERENCE BETWEEN CALCULATED AND
MEASURED VALUES OF ABRASIVE INDEX

Calculated index deduced from	Ak. index		D/hr. index	D/HP index
	D/hr. index	D/HP index	Ak. index	Ak. index
Largest errors (%)	$\begin{cases} +75\% \\ -42\% \end{cases}$	$\begin{cases} +55\% \\ -33\% \end{cases}$	$\begin{cases} +45\% \\ -32\% \end{cases}$	$\begin{cases} +34\% \\ -28\% \end{cases}$
Average error (%)	23%	19%	16%	14%
Number of cases where error exceeds 30%	8	6	6	4
Root mean square of differences between calculated and measured log indices	0.125	0.10	0.085	0.075

It is clear that abrasive indices obtained by the Akron and du Pont tests are not mutually convertible with any degree of exactness.   The errors seem to be somewhat less, however, when the results from the latter are expressed as loss/HP-hr.

Published comparisons of abrasion methods have been studied to see whether a similar conclusion is true of other tests besides using the Akron and du Pont machines.   It is found that, as in the present experiments, abrasive indices, determined by different methods, are not exactly related, so conversions from one method to another involve errors, which, however, are usually less than those shown in Table 2.   The relevant data are summarized in Table 3.   As the errors might be expected to be greater among rubbers that vary widely in abrasion-resistance, Table 3 includes figures showing the variation between rubbers.   The figures tabulated, which are all in terms of the logarithm of the abrasive index, are therefore: (1) *variation between rubbers:* for each rubber the log indices by all the methods have been averaged, and the variation among these averages calculated in the usual way as standard deviation; (2) *dis-*

<div align="center">TABLE 3</div>

No. of rubbers tested (a)	Methods used (b)	(1) Variation between rubbers	(2) Discrepancy	Notes	Reference
4	A, G, J, J2, S, U	0.36	0.22	(c)	4
32	A, D	0.14	0.12	(d)	—
5	D, J, K, R, U	0.075	0.11	(e)	7
7	D, G2, R	0.055	0.065	(f)	8
5	D, K, R	0.08	0.045	(g)	9
4	A, D2	0.14	0.04	(g)	10
4	D, J, R, U	0.16	0.035	(h)	11
10	D2, R	0.15	0.035	(g)	12

(a) Including that used as standard in calculating abrasive indices.

(b) A: Akron; D: du Pont; D2: Dunlop; G: Goodrich; G2: Goodyear; J: New Jersey Zinc, with lifts; J2: as J, but without lifts; K: Kelly; R: road test on tire; S: sand-blast; U: U.S. Rubber Co.

(c) One very soft rubber, giving extremely divergent indices by different methods, has been omitted. Variation between rubbers is only 0.12 if the standard rubber is excluded.

(d) Present experiments; mean of D/hr. and D/HP results used for method D.

(e) One rubber, apparently deficient in accelerator, has contributed largely to the error.

(f) All rubbers were first-grade treads.

(g) All tread rubbers.

(h) Tread rubbers with various proportions of reclaim.

crepancy: this is a measure of the average difference between calculated and measured log indices for the same rubber.

The sets of data in Table 3, arranged in order of decreasing error (discrepancy), show that the error varies greatly from one set to another. The following conclusions are indicated by Table 3 and the original data on which it is based.

(1) Some of the error values from published data are greater and some less than those deduced from the present experiments. Percentage error figures such as those shown in Table 2 would be correspondingly greater or less than these figures; thus, under the most favorable conditions, as represented by the bottom two lines of Table 3, the average error in calculating an abrasive index from results of another method, would be only about 6 per cent.

(2) The magnitude of the error does not depend on how widely the rubbers vary in abrasion-resistance, though it is significant that all the sets of tire-tread rubbers[6-10] give small errors, and that the most variable set of rubbers[4] has given the biggest error.

(3) There is no indication that any one type of abrasion machine gives abnormally discrepant results.

(4) The error in comparing road tests with a laboratory method is about the same as in comparing two laboratory methods; consequently, the relative tread wear of rubbers can be predicted by a laboratory test about as accurately as the result from one laboratory test can be predicted from the results of another.

Akron–du Pont relation among rubbers of individual manufacturers

An interesting observation arising from Table 1 is that among the rubbers of certain manufacturers the Akron index calculated from du Pont results is almost always greater than that measured directly on the Akron machine, whereas the rubbers of other makers show the opposite. This is illustrated in

Figure 1 by the fact that all the points for some makers lie above the line AB, while those for other makers lie below. These differences are set out more fully in Table 4.

It thus seems that the products of certain makers, *e.g.*, I and II, are characterized by an unusually high ratio between du Pont and Akron indices, while those of others (V, VI, VII) give unusually low ratios. Mathematically this means that the constant at the right hand of Equation (1) or (2) may vary from one maker to another. The reason is presumably that the du Pont/Akron relationship varies according to the type of rubber compound, and that

TABLE 4
RUBBERS GROUPED BY MANUFACTURERS

Manufacturer	Number of rubbers for which the calculated Ak. index is				Average difference (%) (calculated-measured)	
	greater than measured index		less than measured index			
I	4;	4	0;	0	45;	35
II	4;	4	1;	1	15;	15
III	4;	3	1;	2	5;	3
IV	2;	2	3;	3	− 5;	− 3
V	0;	0	5;	5	−30;	−20
VI	1;	1	4;	4	−25;	−15
VII	0;	0	2;	2	−25;	−20

NOTE.—The first and second numbers in each pair relate to D/hr. and D/HP indices, respectively.

rubbers made by the same manufacturer tend to be alike in formulation. It follows that among the products of any one manufacturer the conversion of du Pont to Akron indices, or *vice versa*, can be made more accurately than among rubbers generally, the discrepancies being only about two-thirds as large as those shown in Table 2.

RELATION OF LABORATORY TESTS TO SERVICE WEAR

In considering abrasion tests it seems logical to regard service wear as equivalent to one other form of test, since any particular class of rubber product, *e.g.*, tire treads, heels, or conveyer belt covers, is subjected to one type of abrasive action. The ideal test would exactly reproduce this action, but for the existing forms of test it is safest to assume that this is not the case, and that the mechanism of abrasive wear is likely to differ at least as much between a laboratory test and service wear as between different laboratory tests.

On this assumption, the errors that arise in assessing service wear from tests on a laboratory machine are likely to be of the same order of magnitude as those in calculating an abrasive index for one machine from that measured on another; this is confirmed by conclusion (4) above. If, therefore, rubbers are accepted or rejected according to a datum line index figure, the decision will sometimes be wrong; thus, judging by the present results on sole and heel rubbers, a wrong decision may be expected roughly once in five times. A surer guide could be obtained by using two or more different methods, and accepting only the rubbers that pass the datum line by all the tests.

It follows also that quantitative estimates of service durability may be in error by amounts of the same order of magnitude as indicated in Table 2. Although these errors appear large, the chances of a really serious wastage of rubber are small; thus, according to the present results there would be less than

1 chance in 200 that a rubber accepted by a laboratory test as just satisfactory would give only have the expected service life. It is perhaps more useful to consider what would be the average overall error in dealing with a large number of, say, soling rubbers. The following cases may be considered: (1) that all rubbers are accepted for use without regard to their abrasion-resistance; (2) that a laboratory abrasion test is made, and a datum line fixed that divides the rubbers into two equal groups, only the better group being accepted; (3) as (2) but a hypothetical laboratory test is used that exactly reproduces service wear; this is, of course, the ideal case.

On the basis of the results in Table 1 (averaging the D/hr. and D/HP indices for convenience) it can be shown that the average abrasion resistance of the rubbers approved by the ideal procedure (3) might well be some 21–33 per cent higher than if procedure (1) were followed; the higher or lower figure would have to be taken according as the Akron or du Pont test gives the truer measure of service wear. Rubbers accepted by procedure (2) would have an average abrasion resistance 16 to 22 per cent higher than (1). In other words, the laboratory methods, imperfect as they are, make it possible to secure some two-thirds or three-quarters of the advantage obtainable from an ideal testing system. This degree of efficiency is obtained even though the discrepancies between methods are in this case relatively large (error, in Table 3, being 0.12); in the best case shown in this Table (error 0.035) this efficiency reaches about 96 per cent, meaning that the laboratory test is practically as good as the test of service wear.

SUMMARY

Abrasion tests on several sole and heel rubbers have been made on the Akron and du Pont machines to determine whether the same abrasive index (abrasion-resistance relative to a standard rubber) is given by both methods. The following conclusions are drawn from the results.

(1) The two methods do not give the same abrasive index for the same rubber; a study of published data shows that this is true of at least some other abrasion test methods. In using an abrasive index to specify or control the quality of manufactured articles it may, therefore, be necessary to establish a separate index figure for each type of machine used.

(2) Broadly speaking, the higher the abrasive index of a rubber by any one method, the higher is its indices by other methods, so abrasive indices can be converted approximately from one method to another by using a suitable factor or conversion formula; a formula for interconverting Akron and du Pont results is given.

(3) Such conversions from one method to another are only approximate, however, because indices determine by different methods are by no means exactly related. The magnitude of the errors involved is indicated and discussed; in the present experiments the average discrepancy between an index measured directly and that calculated by the formula from the index given by the other machine, is about 20 per cent; corresponding figures from published data range from about 6 to 40 per cent.

(4) Errors similar to those just mentioned, occur in predicting the relative service wear of different rubbers from laboratory abrasion tests. Although these errors seem large, the chances of a rubber that gives a satisfactory test result proving really poor in service are small.

(5) The adoption of any system that prevents unsatisfactory material being put on the market is a valuable means of saving rubber. On the basis of the present results with the Akron and du Pont machines, it can be shown that by the application of a laboratory abrasive index test the resultant saving of rubber is at least two-thirds of what would be saved if acceptance or rejection could be based on actual service wear results—an ideal but impracticable procedure.

(6) There is evidence that among rubbers of similar composition, *e.g.*, sole and heel rubbers made by any one manufacturer, abrasive indices obtained by different methods are more closely related than among rubbers in general. For control and development work within the factory, therefore, the abrasive index system should prove more satisfactory than when applied to a varied assortment of rubbers of unknown composition.

(7) Abrasion methods may differ in their power of discriminating between rubbers; thus, in the present experiments, the Akron test shows wider differences in abrasive index than the du Pont test, although the latter has the higher power of discrimination.

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QUALITATIVE DETECTION OF TITANIUM DIOXIDE IN RUBBER *

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Titanium dioxide, either as such or in the form of the composite titanium whites, is now used to such an extent as a rubber pigment that a test for titanium is frequently necessary in the analysis of a compounded rubber. Owing to the insoluble nature of titanium dioxide, troublesome fusions are required to detect it by the normal qualitative tests in the ash remaining when a rubber is incinerated. The following method is offered as a quick and easy means of detecting titanium.

A small portion (about 0.01 gram usually suffices) of the ash from the sample is placed in a clean glazed 15-cc. porcelain crucible. One drop of concentrated sulfuric acid is then added, and the whole is heated on a hot plate for 30 seconds, *i.e.*, until most of the acid is evaporated. The crucible is allowed to cool, and 2 drops of 6 N sulfuric acid added, followed by 1 drop of a 5 per cent aqueous solution of the sodium salt of chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid). A brownish red to purple coloration is obtained if titanium be present. In place of the chromotropic acid, 1 drop of 10-volume hydrogen peroxide is added in a second test, when the well-known golden yellow color is obtained.

The test by means of chromotropic acid is adapted from "B.D.H. reagent for spot tests," published by British Drug Houses, Ltd. The hydrogen peroxide test is already in use in a different form in normal qualitative analysis.

Mercury, silver, uranium, and ferric iron may interfere with the chromotropic acid test, and vanadium with the hydrogen peroxide test, but as the only mercury compound used in rubber is vermilion, which volatilizes during incineration, the possibility of any of these elements except ferric iron being present in a rubber ash is very remote. As ferric iron does not interfere with the hydrogen peroxide test, its presence does not render the present method invalid. Two tests should be made, one with chromotropic acid and one with hydrogen peroxide, and two positive results should place the matter beyond doubt.

Tests have been made by the new method on several rubbers with and without titanium dioxide, and on a set of mixed pigments comprising titanium dioxide together with the common inorganic pigments (antimony sulfide, cadmium sulfide, chromic oxide, ferric oxide, ultramarine, and vermilion). In every case the presence or absence of titanium was correctly indicated by both the chromotropic acid and hydrogen peroxide tests. Tests have not been made to determine whether the small amounts of titanium present in certain minerals, *e.g.*, clay, are detected by this method.

When a crucible has been used for this test, care must be taken to ensure that it is properly cleaned before reuse. Boiling a little concentrated sulfuric acid in it has been found efficacious.